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[54] **PHOTOSENSITIVE SILVER HALIDE LAYERS AND PROCESS**

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[*] Notice: The portion of the term of this patent subsequent to Nov. 27, 1990, has been disclaimed.

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[51] **Int. Cl.**..... **G03c 5/00**

[58] **Field of Search**..... 96/36.2, 48 PD, 86 R, 27 R, 96/50 R, 33

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[57] **ABSTRACT**

This disclosure concerns a process of producing photographic images by photoexposing a photosensitive silver halide layer of less than two microns thickness and subsequently physically developing the exposed layer to obtain a visible image. The preferred silver halide layers are of a thickness of less than one micron. The resulting photo-images are characterized by extremely high resolution, especially resolution required for holographic imaging and reproduction. Additionally, the images are adherently bonded to the film substrate.

There is a need for silver halide layers which give high order resolution, for example as required in holography. Additionally, particularly in the production of photographic film, printing plates, nameplates and electrical printed circuits and components, there is need for silver halide layers which yield metal images that are adherently bonded to the layer substrates.

The present invention provides a solution to the said needs and additionally provides this solution by way of extremely rapid and facile processing chemistry.

17 Claims, No Drawings

PHOTOSENSITIVE SILVER HALIDE LAYERS AND PROCESS

This is a division of application Ser. No. 45,927, filed 6–12–70, now U.S. Pat. No. 3,775,114.

DESCRIPTION OF THE INVENTION

This invention relates to the production of photographic metal images by physical development of very thin light-sensitive silver halide layers of thicknesses of less than about 2 microns and preferably less than about 1 micron. The silver halide is preferably dispersed in a binder. Additionally, the invention provides a new process for producing the very thin, light-sensitive layers for use in producing photographic metal images by physical development, as well as the products produced thereby.

The very thin, light-sensitive silver halide layers are produced by coating a low solids emulsion preferably containing less than 10 percent and more preferably less than 5 percent total solids on a suitable substrate to obtain very thin silver halide layers, the amount of the silver halide preferably being from about 100 and more preferably from about 10 to about 20 grams/per liter of the emulsion. It is necessary only to have sufficient silver halide present to obtain a latent image upon exposure which is amplifiable by physical development, preferably to produce good image adhesion to the support. The coating emulsion is made up using conventional binders, such as gelatin, polyvinyl alcohol and the like, with the selected silver halide, the ratio of silver halide to binder being from as high as 20/1 to as low as 1/20 but preferably, for best results, from about 3/1 to about 1/3. Slow, fast, or intermediate photographic response silver halide layers can be formed by control of the particle size as is generally known and well documented in the literature. The silver halide emulsion can be stoichiometrically balanced or contain excess of either silver ions or halide ions depending on the end use or the shelf-life requirements, as is also well known. For example, for slow photographic response, large excesses of halide in the emulsion are avoided since these favor larger silver halide particle size through ripening and, as is well known, the larger particles lead to fast photographic response.

The production of photographic metal images is accomplished by contacting the very thin, light-sensitive layer after photoexposure with a physical developer. As is generally well-known, a physical developer is composed of a reducible metal ion and a reducing agent therefor. In physical development, the reducible metal ion, after reduction, forms the greater part of the developed photographic image, rather than the silver halide of the photosensitive emulsion, although the resulting image does contain at least light-reduced silver particles and may contain additional silver depending on the reducing system employed. In other words, the silver halide of the photosensitive layer hardly contributes to the final visible image. Such physical development is distinguished from the usual chemical development associated with silver halide photoprocessing which is predicated on the formation of visible images solely utilizing the silver of the silver halide in the photosensitive layer. Classically, the silver halide in the photosensitive layer is solubilized using complexing agents such as soluble thiosulfates or thiocyanates and the image is formed by reduction of the solubilized silver halide using conventional reducing agents, i.e., developers.

The use of very thin, light-sensitive silver halide layers provides substantial advantage in many areas of photographic production of visible images. The said layers permit ready and facile physical development to produce very desirable properties in the metal images obtained. For example, the metal images are readily produced in a form very desirable for printed circuit and planographic master production, i.e. the image obtained can be more readily produced as a lustrous continuous and conductive metal image than can be obtained with thicker photosensitive layers. Further, with the aforesaid very thin photosensitive layers, after physical development, the image produced is more adherently bonded to the substrate when compared to images produced with layers of 2 microns or higher thickness. This is of particular advantage when the substrate is metal plate. In producing printing plates, a strongly adherent continuous lustrous metal image is more readily obtained then with thicker photosensitive layers. The thin, light-sensitive silver halide layers of this invention also give rise, on development, to exceptionally thin metal images which are especially suitable where distortion due to layer thickness or metal image thickness is to be avoided as in photogrammetry, as in production and reproduction of holographic images where high resolution is an absolute requirement. The present new thin layers give images which are of exceptionally high resolution.

The use of such thin photosensitive layers as in the present invention also leads to considerable advantage in the packaging of film where, conveniently, the film is usually packed in rolls, with the present film requiring less space than prior art films designed for the same use. Thus, in the same package space, more of the present film can be made available than with conventional film.

Additionally, the fixing and drying time is significantly improved. This is especially important, for example, in the high speed processing of photographic film (e.g., at speeds of 100 feet/min. or greater). An additional advantage is that the manufacture of the film is simplified since the photosensitive layer drys and sets more readily and has less rheology problems than with film having thicker layers. The film can be more economically manufactured since conventional coating equipment can be used such as film subbing equipment rather than the relatively slow and more costly photographic coating equipment.

One of the more important advantages of the photosensitive medium of this invention is that it has the capability of being very high photographic speed such as for taking pictures in a camera and also capable producing extremely high resolution and at the same time having the capability of high or low gamma images. This unusual combination of properties makes possible improved high resolution original aerial photographs, forming a printing plate by exposing directly onto a photosensitive plate from a computer-driven CRT or other exposure device. Photographic film having improved archival quality is also possible due to the excellent adhesion possible between the image and the support. Thus, abrasion which might remove the binder does not necessarily remove the image from the film.

PREFERRED EMBODIMENTS OF THE INVENTION

The silver halide employed is that which is conventionally used in photography and is made in the conventional way, i.e., by reaction in aqueous systems of soluble silver salt such as silver nitrate or sulfate and a soluble alkali metal halide, such as sodium chloride, sodium bromide or sodium iodide, or corresponding potassium salts. The formation of the particles of silver halide can be controlled to permit any desired particle size, ranging from as little as 30 to 50 Angstrom units up to conventional particle size. Preferred methods are those which encourage fine particle size, usually less the 0.5 microns. For general convenience, such fine particle size is obtained by using systems of low solids content, preferably at approximately 5 percent total solids (including the weight of silver halide and the binding agent) and rapidly mixing the soluble alkali metal halide solution with the soluble silver salt solution, usually at about room temperature, for convenience.

The binder employed can be any of those conventionally used in forming silver halide emulsions. Preferably, the binder should be wettable by aqueous solutions to a sufficient degree to permit rapid processing of the exposed layer. Preferred binders are the usual gelatin, so common in silver halide films, polyvinyl alcohol, polyacrylates, including polyacrylic acids, casein and the like. The use of polyvinyl alcohol is especially preferred where fine particle size of the silver halide is desired since the binder apparently discourages ripening, i.e., growth of the silver halide particles which occurs on standing.

The binder, of course, is added to the aqueous system used to form the silver halide particles, as a matter of convenience. In addition, other materials can be added to the binder-aqueous system as desired to obtain specific effects in the photosensitive layer during or after exposure. For example, sensitizing dyes, thiourea, toners, mercuric salts or the like can be added for their known photographic effects, e.g., thiourea to assist in formation of black photographic images, and the sensitizing dyes to alter the spectral response of the layer on photoexposure.

After preparation, the emulsion is then coated on a substrate. The coating process can be any of those commonly employed, e.g., air knife, roller coating or similar such coating means. With proper settings, a coating weight of about 0.5 grams per square meter can be readily attained and gives a uniform layer of about 0.5 microns. By adjustement, thinner layers, e.g. 0.2 – 0.3 microns and even lower, can be made. Thicker layers up to one micron and higher present no problem to those skilled in the art. The optimum layers are produced with a ratio of silver halide to binder of from about 3/1 to about 1/3.

The preferred thin layers, i.e., of thickness below one micron, usually contain as silver halide, approximately 0.3 grams of silver per square meter.

The physical developers which are preferred are so-called stabilized physical developers, particularly those which are most effective at acid pH value, i.e., below pH 7. Especially preferred are the so-called mono-bath physical developers which are stabilized. Monobath physical developers consist of a single solution of reducible metal ion and the reducing agent therefor. On prolonged use, there is apparently a tendency to formation of undesired side products. Stabilized monobath physical developers are known in the art and usually include surfactants or similar such materials which prolong the life of the physical developer. One of the basic problems with physical developers is the tendency toward decomposition with formation of insoluble materials that contaminate photographic emulsions or otherwise are undesirable in terms of their adverse affect on the acceptability and/or aesthetics of the photographic image. The surfactants apparently minimize such decomposition, i.e., stabilize the physical developer.

The optimum results attainable with the physical developers is at pH values below 7, i.e., in acid media, usually at about pH 1–5. Higher pH values should be avoided because of the possible adverse effect on the surfactants which are sensitive to high pH values.

In the physical developers employed, the reducible metal ion is usually of a metal at least as noble as copper, e.g., silver, copper, gold, platinum, palladium and the like. However, other metal ions such as nickel and tin can also be used, with appropriate reducing agents. Reducing agents for copper, silver and like noble metal ions are readily determinable and are fully described in the literature.

A particularly effective monobath physical developer is composed of silver ion and, as reducing agent therefor, the ferrous-ferric ions developer which is well-known to the art.

For best results, the monobath physical developers are usually prepared immediately before use to increase the useful life of the system. The surfactants are added during fromation of the monobath to obtain maximum stabilization.

The physical developers may contain additional materials which assist in formation of the desired type of photographic image. Thus, for example, complexing agents for the metal ion to be reduced may be present, or toners which affect the physical appearance of the resulting photographic image.

In lieu of the described monobath physical developers, there may be used separate solutions of the reducible metal ion and the selected reducing agent. For example, the physical developer can be made up of separate solutions of silver ions, and Metol. The exposed layer is first immersed in the silver ion solution and subsequently in the Metol solution. The results obtained are quite acceptable but the separate steps are undesirable for obvious reasons of time and labour waste. Additionally, the results are not always as reliable with reference to the reproducibility, desirable photographic image characteristics as those attainable with monobath physical developers, especially in stabilized form.

One or both of the oxidizing and reducing agent components of the developer may be present in the photosensitive medium prior to exposure, if desired.

The physical developer, irrespective of monobath, separate solutions or stabilization, can be applied to the photosensitive layers in the from of viscous solutions or gels with essentially the same results as the liquid systems. The efficiency of viscous solutions, and particularly gels, make these forms of the physical developer particularly desirable in commercial use of the present new thin photosensitive layers.

Alternately, the image forming materials (physical developer) may be incorporated in the photosensitive layer of this invention. Thus, a decomposable metal salt such as silver EDTA may be incorporated in the photosensitive layer as described in copending U.S. application Ser. No. 45,909, filed June 12, 1970 in the name of John Manhardt, entitled "Print-out Processes and Imaging Media Therefor," now Pat. No. 3,794,496. Also, an oxidizing agent and a reducing agent such as described in U.S. Reissue Pat. No. Re. 26,719 may be utilized as the image forming materials in the photosensitive medium. The advantages of a high resolution print-out photographic system requiring no wet processing are apparent.

The sensitometry of the present thin films can be altered to meet a desired photographic use. For example, the photoresponse and gamma can be changed in the emulsion if different mixtures of silver halides are used, and/or by increasing the silver halide particle by allowing ripening to take place. Gamma can be controlled by addition of known materials, e.g., cadmium salts, or by regulating the amounts of surfactants and/or pH of the physical developer.

In a particularly preferred form of the invention, the exposed thin layer is first chemically developed, e.g., by contact with known chemical developers such as hydroquinone, metol, and the like, after which physical development, as hereinbefore described, is used to obtain the final image. Such chemical development usually leads to a faint silver image which is then amplified by physical development. The intermediate chemical development, followed by physical development, results in an increase in the effective speed. The higher effective speed is accompanied by a slight decrease in gamma. The intermediate chemical development is particularly desirable to obtain continuous tone images in the physically developed film. In addition, when the metal ions of the physical developer are other than silver ions, the intermediate chemical developement step gives substantially better results in the physical development step.

The intermediate chemical development of the exposed thin silver halide layer leads to a more adherent metal image obtained by physical development. This adherence of the metal image is, of course, in reference to the substrate, and, in photographic media comprising a metal substrate, this improved adherence to the metal substrate is especially desirable, particularly in making printing plates, nameplates, electrical circuits, and the like.

In another preferred form of the invention, the thin, photosensitive layer is applied to a hydrophobic substrate such as cellulose acetate or a polyester film base, e.g., polyethylene terephthlate, without the use of the subbing layer or with a single subbing layer rather than the two or more which is so common to such substrates. Furthermore, the coatings can be applied with conventional coating equipment such as equipment for applying subbing layers rather than expensive and slow photographic coating equipment. The applied silver halide layer is comprised of a binder principally consisting of material normally designated "subbing binder," or subbing material which preferably comprises a mixture of a hydrophobic and hydrophilic material such as a mixture of gelatin and a synthetic polymer. The "subbing binder" or subbing material may also comprise solely a synthetic hydrophilic binder material capable of adhering to the polyester or cellulose triacetate support or such a support having a single subbing layer.

The subbing material is a material which will allow development to take place in. Emulsion polymers or combinations of these polymers with gelatin are preferred. Examples of such subbing materials are vinylidene chloride copolymers, acrylate polymers and copolymers polyvinyl acetal polymers, and polybutadiene copolymers. Suitable such copolymers include the vinylidene chloride copolymers containing at least 35 percent by weight of vinylidene chloride, e.g., the poly(vinylidene chlrodie and acrylic or methacrylic ester or nitrile and itaconic acid) compounds described in Alles and Saner U.S. Pat. No. 2,627,088, the polyisocyanates and polyisothiocyanates described in Saner U.S. Pat. No. 2,698,242, the mixtures of (a) polyester of ethylene glycol, terephthalic acid and polyethylene glycol or saturated aliphatic dicarboxylic acid, soluble in $CHCl—CCl_2$, and (b) organic polyisocyanate or polyisothiocyanate described in Saner U.S. Pat. No. 2,698,241 and the polyesters of aforesaid item (a) described in Alles and Saner U.S. Pat. No. 2,698,239. The various copolymers of vinylidene chloride mentioned are described in U.S. Pat. No. 2,627,088, including methods of preparation, and the said patent is incorporated hereby by reference for the said disclosure. Additional subbing materials are the butadiene copolymers as described in Belgium Pat. No. 721,469.

An especially preferred embodiment is a sheet material wherein the binder additionally comprises gelatin.

The following examples further illustrate the invention. Unless otherwise indicated, all parts are parts by weight.

Example 1

A 5 percent solution of polyvinyl alcohol (PVOH) is prepared by slowly adding the resin powder to distilled water at room temperature with rapid stirring. The temperature is slowly raised to 95° C. while maintaining rapid agitation, and held at 95° C. for about 0.5 hour.

The following solutions are prepared using the 5 precent PVOH solution thus prepared:

Solution A		Solution B	
Distilled H_2O	84.0	Distilled H_2O	84.0
10% aq. NaCl	30.9	10% aq. $AgNO_3$	81.5
5% PVOH	14.0	5% PVOH	14.0

(Solution B is not prepared until immediately before the described use, i.e. freshly prepared before mixing with Solution A.)

Solution A is added to Solution B under good agitation within about 5 seconds total addition time, at room temperature. The mixture is then sonified (Bronson Sonifier) for 4 minutes at about 100 watts. Then, 248 parts of 5 percent PVOH solution is added to the mixture under good agitation and agitation is continued for about 5 minutes thereafter. Subsequently, the mixture is filtered through a 5 micron bag to obtain an emulsion of the following characteristics:

Emulsion Constants:

1:2 rates of silver chloride to PVOH
10 percent excess chloride
4.5 percent total solids

12.4 g. silver chloride/liter
pH = 5.9 to 6.2
viscosity = 6 to 8 cps

The emulsion can then be coated on a substrate by either air knife, roller coating or similar coating means. Good results are obtained using a roller coater with hard rubber rolls. With proper settings, a coating weight of 0.5 g./m² can readily be obtained.

A polyester film having a single vinylidene chloride copolymer subbing layer is so coated and thoroughly dired by heating at about 27°C for 10 minutes. The coated film is then exposed and developed in the following stabilized physical developer:

Solution I	Ferrous Ammonium Sulfate	78.4 gms.	bring to 1
	Ferric Nitrate	32.3 gms.	liter with
	Citric Acid	80.0 gms.	distilled water
Solution II	Distilled Water	100.0 gms.	
	Synthrapol N	1.0 gms.	
	Armac 12D	1.0 gms.	
Developer	Solution I	125.0 gms	
	Solution II	25.0 gms	
	3N Silver Nitrate	6.0 gms.	

A lustrous, coherent, metallic image is obtained on the film.

Example 2

The following solutions are prepared as in Example 1:

Solutions

A		B		C	
Distilled Water	92.0	Distilled Water	92.0	30% Phenyl Mercuric Acetate	1.15
10% NaCl	30.9	10% $AgNO_3$	81.5		
5% Lemol 16-98	206.0	5% Lemol 16-98	206.0		

The solutions are mixed in the following order: Solution A is added to Solution B, Soluction C is added to the mixture, and the mixture is stirred and filtered as in Example 1, to obtain and emulsion of the following characteristics:

Emulsion Constants
1.3 Silver Chloride to Binder
10 percent Excess Chloride
4.5 percent Total Solids
9.7 Grams Silver Chloride per Liter
1 percent Mercury on Binder Solids
pH = 7.7 to 8.0
Viscosity = 6 to 8 cps.

The combined solutions are used to coat a subbed, polycoated paper stock with a roller coated and the paper then is exposed and developed as in Example 1. The silver chloride particle size (average) ranges from 50 to 200 A. and the layer thickness is about 0.1 micron.

Example 3

An emulsion containing 8 percent excess silver at a total solids content of 4.4 percent is prepared from the following solutions:

Solution I		Solution II	
18 cc.	3N $AgNO_3$	3 gms.	NaCl
210 cc.	H_2O	210 cc.	H_2O
72 gms.	Lemol 16-98 (10%)	72 gms.	Lemol 16-98

Solution II is added to Solution I rapidly with stirring and the mixture is then sonified for 5 minutes. The emulsion is then used to coat any desired substratefilm, paper, aluminum metal — at a coating weight of about 0.5 g/m², i.e. at a thickness of 1 micron or less.

The coated substrate is then exposed and process as in Example I.

Example 4

The following solutions are prepared:

Solution A

Distilled H_2O	85	ml.
Sodium Chloride	6.67	gms.

Solution B

Distilled H_2O	250	ml.
Silver Nitrate	15	gms.
K&K Inert Gelatin	20	gms.
Formaldehyde	1	gm. (3%)

Solution A is poured into Solution B at 60° C. and vigorously stirred for 3 minutes. After cooling to 30°C. the mixture is coagulated by rapid addition of methanol and distilled water 1:1 cooled to −12°C. The mixture is stirred until coagulum forms and the liquid clears. The coagulum is removed and cut into small "noodles" which are washed twice with cold distilled water. The coagulum is then dissolved in water to form one liter aqueous emulsion which is then used to coat substrates as in the previous examples.

Example 5

The procedure of Example 2 is repeated with the added step of chemical development prior to the physical development. The chemical development is by immersion in a standard silver halide developer, e.g. Kodak D-19 or D-76, to obtain a faint silver image.

After physical development, the resulting image is more detailed than that of Example 2, i.e. lower gamma.

Example 6

The procedure of Example 5 is repeated substituting a metal substrate for the paper substrate and utilizing the following physical developer:

$CuSO_4$ (10% aq.)
Na_4EDTA (10% aq.)
NaCl

The resulting image is adherently bonded to the substrate.

Example 7

The procedure of Example 1 is repeated with the added step of chemical development as in Example 5, i.e., prior to physical development, and the resulting is of greater detail than that obtained in Example 1. The photographic gamma is about 1.5 whereas that of the Example 1 image is greater than 3.

Example 8

The procedure of Example 1 is repeated with the ex exception that the physical developer is the following solution:

$CuSO_4$
Ascorbic Acid

Example 9

The procedure of Example 1 is repeated with the exception that the physical developer is the following solution:

$AgNO_3$
Metol
Citric Acid

Comparable results are obtained.

Example 10

The procedure of Example 1 is repeated to form a printed electrical circuit consisting of silver.

The printed circuit is then amplified to an additional thickness of 1–5 mils. by electrolytic deposition of copper using a conventional copperizing bath, e.g. $CuSO_4H_2SO_4$ solution at coating electrical current.

The metal printed circuit is adherently bonded to the substrate.

Example 11

The procedure of Example 2 is repeated using a brush-grained anodized aluminum sheet as substrate in lieu of paper.

The resulting plate is then wiped with a dispersion of mercaptobenzothiazole (e.g.) phosphoric acid (5 ml. 85 percent) and dodecylammonium chloride (0.5 g.) in one liter of water. The silver image will now accept lacquer or ink depending on whether it is to be used as a color image (by inclusion of color in the lacquer) or as a printing plate.

The metal image is adherently bonded to the aluminum substrate.

EXAMPLE 12

In a reaction flask equipped with a stirrer, a nitrogen inlet, a dropping funnel, and a condenser are placed 10 liters of water and 2.88 liters of a 10 percent aqueous solution of the sodium salt of sulphonated dodecyl benzene. Then the reaction flask is rinsed with nitrogen and the liquid is heated to 60°C. In another flask are placed successively 800 ccs of isopropanol, 144 g of N-vinyl-pyrrolidone, 108 g of n-butyl acrylate, 830 g of N-tert.-butylacrylamide and 2,520 g of vinylidene chloride. The mixture is sitrred and brought to dissolution by gentle heating.

Through the dropping funnel a solution is added of 21.6 g of ammonium persulphate in 400 ccs of water. Immediately pumping of the monomer solution into the reaction flask is started. The rate of pumping is such that after 75 min. all the monomer solution is pumped over. Together with the monomer solution a further amount of ammonium persulphate solution is added dropwise (64.8 g in 1,200 ccs of water). During the whole reaction period the temperature of the mixture is maintained at 60°C while refluxing. After all the monomer has been added, again an amount of 21.6 g of ammonium persulphate dissolved in 400 ccs of water is added at once. After refluxing, stirring is continued for another 30 min. at 60°C, whereupon the reaction mixture is cooled to room temperature.

In order to precipitate the copolymer of vinylidene chloride, N-tert.-butylacrylamide, n-butyl acrylate, and N-vinyl-pyrrolidone (70:23:3:4), the latex formed is poured into a mixture of 40 liters of 10 percent aqueous sodium chloride solution and 40 liters of methanol while stirring. The fine grainy precipitate which is obtained is repeatedly washed with water and finally dried.

An amount of 2.5 g of the vinylidene chloride copolymer formed above are dissolved in a mixture of 90 ccs of butanone and 10 ccs of nitroethane. The solution obtained is warmed to 25°C and coated on a plate of polymethyl methacrylate in such a way that 0.75 to 1.0 g of copolymer is present per sq.m. This layer is dried at room temperature.

A copolymer latex is prepared as follows:

In a 20 liters autoclave are placed successively:	
water boiled under nitrogen	10.2 l
10% aqueous solution of oleylmethyl-tauride	0.6 l
10% aqueous solution of the sodium salt of heptadecyl-disulphobenzimi-dazole	0.6 l
azodiisobutyronitrile	6 g
methyl methacrylate	1500 g
butadiene	1500 g

After sealing of the autoclave, the strongly stirred emulsion is polymerized for 6 hr. at 60°C. This polymerization is slightly exothermic for a short while. Then the pressure drops rapidly. The polymerization is finished under reduced pressure. The latex of the copolymer of butadiene and methyl methacrylate (50:50) is then freed from residual traces of monomer by blowing at 60°C and under a slight vacuum an air current above the latex. Then the latex is cooled and filtered.

The above latex copolymer is now used to prepare an emulsion of the following composition:

Solution A		Solution B	
Distilled H_2O	84.0	Distilled H_2O	84.0
10% aq. NaCl	30.9	10% aq. $AgNO_3$	81.5
5% gelatin	14.0	5% gelatin	14.0

Solution A is added to Solution B with good agitation over a time period of approximately 5 to 10 seconds. Then, 248 parts of a 5 percent latex copolymer prepared above is added to the mixture under good agitation. The agitation is continued for 30 minutes. The

emulsion is then filtered and is ready for coating. The coating may be applied by an air knife, roller coating or other means. The coat weight should be kept at approximately 0.5 grams per square meter or below.

The subbed polyester film having a single vinyl copolymer subbing layer is so coated and thoroughly dried. The coat of the film is then exposed and developed as described in Example 1.

Example 13

An emulsion is prepared as described above in Example 12 except that the latex emulsion polymer used is either AC–22 or AC–33 as obtained from Rohm & Haas. The emulsion is coated to an identical coat weight and manner as in Example 12 and is exposed and processed as described in Example 1.

What is claimed is:

1. A process for producing a printed circuit of an electrically conducting metal image comprising the steps of exposing an imaging medium comprising a photosensitive silver halide layer of less than about 2 microns thickness on a support and contacting the imaging medium to image forming materials comprising a solution of metal ions to thereby form electrically conducting metal image patterns adherently bonded to the support.

2. Process as in claim **1** wherein the silver halide layer is of a thickness of less than about 1 micron.

3. Process as in claim **1** wherein the thickness of the silver halide layer is less than about 0.5 micron.

4. Process as in claim **3** wherein the amount of silver, as silver halide, is about 0.03 g/m^2.

5. A process of producing a printed circuit of an electrically conducting coherent metal image adherently bonded to a support which comprises:

1. forming catalytic nuclei which will cause the reduction and deposition of metal from a physical developer by a process including the step of exposure of an imaging medium comprising a photosensitive silver halide layer of less than about 2 microns thickness on a support; and
2. thereafter depositing sufficient metal on the catalytic nuclei portions of the imaging medium to form said electrically conducting coherent metal image adherently bonded to the support.

6. Process as in claim **5** wherein said support is a metal support.

7. Process as in claim **6** wherein said photosensitive silver halide layer has a thickness of less than about 0.5 micron.

8. Process as in claim **6** wherein the catalytic nuclei image formed by exposure of the photosensitive silver halide layer is contacted with a chemical developer to develop a silver image followed by contact with a physical developer comprising a solution of reducible metal ions and a reducing agent for these metal ions.

9. Process as in claim **6** wherein the depositing of metal is conducted by first contacting with an electroless metal plating bath comprising a solution of metal ions followed by contacting with an electrolytic copper plating bath to produce a conductive copper image having a thickness from about 1 – 5 mils.

10. Process as in claim **6** wherein the photosensitive layer has a thickness of less than about 0.5 micron and wherein the metal deposited in step (2) is silver, copper, nickel, or tin.

11. Process as in claim **6** wherein the metal is deposited by contacting the imaging medium with image froming materials which comprise ions of a metal at least as noble as copper and a reducing agent therefor.

12. Process as in claim **11** wherein the metal is silver end the reducing agent is ferrous-ferric ions.

13. Process as in claim **6** wherein the metal is deposited by contacting the imaging medium with image forming materials which comprise ions of a metal selected from the group consisting of copper, nickel, tin and silver.

14. Process as in claim **6** wherein the average silver halide particle size is less than about 0.3 micron.

15. Process as in claim **6** wherein the metal support comprises aluminum.

16. Process as in claim **15** wherein the aluminum is grained.

17. Process as in claim **16** wherein the aluminum is anodized.

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