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3,672,899

HIGH CONTRAST PHOTOGRAPHIC MEDIA
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No Drawing. Filed Nov. 2, 1970, Ser. No. 86,376
Int. Cl. G03c 1/00, 1/28
U.S. Cl. 96—88

25 Claims

ABSTRACT OF THE DISCLOSURE

The use of arylmercuric compounds provides improved photographic properties to photosensitive materials, particularly in improving the sensitometric properties of photographic images. Such images show markedly higher gamma values. The arylmercuric compounds are especially effective in so-called low-content silver halide film, especially those containing very thin photosensitive layers.

Field of the invention

This invention relates to the field of photographic media and photographic chemistry.

It has now been discovered that the presence of an arylmercuric compound in the photosensitive layer of a photographic medium substantially improves the photographic efficiency particularly as to image density and contrast. The invention embraces the use of photosensitive materials which are developable to visible images, after photoexposure, by reduction of metal ions or metal compounds to the free metal which forms the visible photographic image. The improvement is especially effective in media of which the photosensitive material is a photoconductor or silver halide. In the latter type of media, a particularly preferred form of the invention resides in the use of arylmercuric compounds in low content silver photosensitive layers, particularly in so-called thin photosensitive layers. Such low-content silver, thin photosensitive layers and media comprising such layers are described fully in commonly-assigned, copending U.S. patent application Ser. No. 45,927, filed June 12, 1970, the disclosure of which is fully incorporated herein by reference.

While the mechanism by which the present invention functions is not completely understood, it is probable that some interaction of the added arylmercuric compound and the photosensitive material occurs during photoexposure. The applicants do not wish to be bound to any particular theory regarding the observed phenomenon but it is apparent that the effect is attributable to the presence of the arylmercuric compound in the photosensitive layer during the photoexposure step since the addition of the arylmercuric compound, after photoexposure, e.g. during photoprocessing, does not improve the sensitometric characteristics of the resulting image. Consequently, it is believed that, in some unknown manner, the arylmercuric compound is affected during the photoexposure step, either to interact with the photosensitive material or to form, itself, some species of active sites or seeds, or both of these, which accounts for the high gamma values observed after photoprocessing. Alternatively, the mercury compound may change the surface charge to permit easier penetration of developers through the lattice. Regardless of any theoretical explanation, the fact remains that the arylmercuric compounds do provide excellent results which are not attainable with the ordinary photosensitive materials alone. For example, with ordinary graphic arts silver halide film, the usual gamma value is from about 4 to about 6, whereas with the arylmercury compound, the

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gamma values observed thus far are usually about 12 and higher. In general, the processed media of this invention are characterized by maximum density in the image areas and, for practical purposes, almost zero density in the non-image areas. This is especially desirable in photographically producing printing plates in that maximum density is obtainable with very few gray steps, usually only 1 or 2 gray steps being encountered.

The arylmercury compounds broadly contemplated are those in which the mercury atom is directly bonded to an aromatic ring structure, i.e. a cyclic structure stabilized by resonance, classically illustrated by the benzene ring. Such compounds include, for example, phenylmercurials such as phenylmercuric acetate, phenylmercuric chloride; phenylmercuric bromide, and the like. Of course, the phenyl group can be replaced by analogous aryl groups derived from naphthalene, anthracene and phenanthrene, as well as heterocyclic compounds such as thiophene, furan, indole, thiazole, thiadiazole, pyridine, and the like, as well as fused ring systems such as benzothiophene and benzofuran. The presence of substituents on the aromatic nucleus is not critical when such substituents do not adversely affect the photographic properties of the photosensitive emulsion, either in the photoexposure or in the photoprocessing, i.e. such substituents should be photographically acceptable. In addition, the arylmercuric compound should not add undesirable color to the photosensitive emulsion. Consequently, unsubstituted arylmercuric compounds are usually preferred.

DESCRIPTION OF PREFERRED EMBODIMENTS

The preferred arylmercuric compounds are those corresponding to the formula:



in which Ar is a monovalent, aromatic nucleus and X is a monovalent negative ion. The preferred aromatic nucleus is phenyl or substituted phenyl, in which the substituents are halogen, lower alkoxy or lower acyloxy. The extent of substitution of such groups on the aromatic nucleus is not critical, so that the nucleus can be mono-, di-, or even trisubstituted without altering the effectiveness of the compound in the present invention. Of course, the substituents on the aromatic nucleus should preferably not give rise to adverse color in the photographic layer and, further, should preferably not react adversely under the conditions of photoprocessing, i.e. the substituents should be photographically acceptable. Such preference also exists with regard to the monovalent negative ion X and the aromatic nucleus each of which should also be photographically acceptable.

The substituent, X, can be any suitable negative ion but preferably is an acyloxy group, especially the lower alkanoyloxy, e.g. acetate, propionate, caproate. Other negative ions which can be used are halide, such as chloride or bromide, nitrate and the like.

The preferred arylmercuric compounds are those which are readily-dispersible in the photosensitive layer and, of course, are photographically compatible with the photosensitive material. At present, the particularly preferred compounds are the phenylmercuric alkanoates, and of these phenylmercuric acetate which is readily available and at the same time economical. For particular photographic results or special effects, a minimum of experimentation by those skilled in the art will permit the selection of appropriate arylmercuric compounds, which selection, of course, will depend, in great part, on the type of photosensitive system utilized.

The preferred photosensitive media are those comprising silver halide as the photosensitive material. Such

photosensitive media are more than adequately described in the literature and are well-known to those in the art. Especially preferred silver halide media are those which contain a low content of silver, as silver halide, in the photosensitive layer, particularly media comprising thin photosensitive layers as described in the aforesaid copending application.

In a preferred form of the invention, the arylmercuric compound is added to an emulsion of the photosensitive material in a binder before the emulsion is coated on a support to form the photographic medium. In this way, uniform distribution of the arylmercuric compound throughout the photosensitive layer is insured. For such purpose, the arylmercuric compound is dissolved in a solvent compatible with the emulsion, e.g. usually a lower alkanol such as methanol, ethanol or propanol, and merely added to the emulsion at any convenient point in the preparation of the emulsion. For example, when the silver halide, e.g. chloride, is prepared in the emulsion by mixture of silver nitrate and a soluble halide, e.g. chloride, it is usually convenient to add the arylmercuric compound after silver halide formation and then mix thoroughly to obtain uniform distribution of both materials in the emulsion. As an alternative the arylmercuric compound can be added to the emulsion system prior to formation of the silver halide.

Although not preferred, the arylmercuric compound can be added to the photosensitive layer after it has been formed on the medium, e.g. by merely immersing the photographic medium in a solution of the selected compound and allowing the layer to absorb by imbibing. Results obtained with media so produced are not of the high order obtained with media produced by the preferred preparative method.

The amount of arylmercuric compound used in the present invention can be varied over wide ranges depending on the desired results and the photosensitive materials employed. A minimum amount of experimentation will permit the selection of optimum concentrations by the mere expedience of preparing media at various concentrations of the arylmercuric compound and selecting the optimum concentration determined. For photographic purpose, it is preferable to select almost minimum effective concentrations of any materials to be added to a photosensitive layer. Since mercuric compounds are known for their toxicity, it is also desirable to minimize the amount of the arylmercuric compound in the photosensitive layer.

For most purposes, it has been found that a concentration of from about 1% to about 7.5% by weight based on the photosensitive material meets such criteria but of course the use of more or less than the said amount will not materially affect the desired results. Generally, from 0.5% up to about 15% by weight will be the most practical range. Usually, the arylmercuric compound at concentrations higher than about 15% causes a noticeable reduction in photographic speed and such high concentrations are thus undesirable in that effect.

The invention contemplates the provision of new photographic media which are characterized by comprising a photosensitive material together with an arylmercuric compound in the photosensitive layer. The arylmercuric compound is preferably uniformly distributed with the photosensitive material in a photosensitive layer on a suitable substrate therefor. The photographic media can be any of those commonly used and known to those skilled in the art. The photosensitive material and the arylmercuric compound are suitably contained in a layer of binding material, such as gelatin, polyvinyl alcohol, polyacrylates and polymethacrylates, as well as copolymers of acrylates and methacrylates. Many such binders are well known in the art and are intended for use in the new media of this invention.

The substrates for the present media include all of the substrates commonly employed such as paper, plastics and metal substrates. For example, cellulose acetate and poly-

ethylene terephthalate can be used for transparent films while metals, such as aluminum and iron, as well as alloys thereof, can be used and are particularly adapted for photographically producing printing plates and printed electrical components, e.g. printed electrical circuits, capacitors, and the like, as well as nameplates and decorative metal plates.

The preferred new photographic media are those in which silver halide is the photosensitive material. Especially preferred are the low silver-content, thin photosensitive layer media described hereinbefore. These media are characterized by a photosensitive layer thickness of less than one micron and preferably less than about 300 millimicrons. Most preferred layer thickness is less than about 100 millimicrons. The silver content of such layers is usually about .05 g./m.² and may be as low as 0.01 g./m.² in the most preferred layer thickness, as described in the aforesaid copending application.

The photosensitive material can also be any of the photosensitive photoconductors, such as described in the patent literature, for example, British specification 1,043,250, incorporated herein by reference. Generally, the preferred photoconductors are compounds of a metal with a non-metallic element of Periodic Group VI. Preferably, these photoconductors are metal oxides or sulfides, such as titanium dioxide, zinc oxide, zinc sulfide, cadmium sulfide, and cerium oxide, among others. Preferred are titanium dioxide, zinc oxide and mixtures thereof.

The photosensitive material and the arylmercuric compound in the selected binder are applied to the substrate using any of the art-recognized techniques, as by use of rollers, in the desired thickness. After drying the photographic media are ready for use. If desired a top coating can be applied to protect the photographic emulsion. Of course, the emulsion can also contain substances commonly employed with the specific photosensitive material, such as dye-sensitizers, sensitizing-metal salts, such as silver and copper salts, photographic reducing agents, and such materials commonly used in photographic emulsions.

The photoexposure step employed is the same as normally used for the selected photosensitive material. The photoprocessing of the exposed medium is also the same as normally employed, the exception in the photoprocessing being a much shorter induction period in image formation which is one of the characteristics of the present new media.

A particularly preferred embodiment of the present invention is the provision of especially effective photographic media for the production of printing plates and electrical components. Especially desirable properties of high density in image areas and little, if any, density in non-image areas makes the new media of the present invention extremely well-suited for the said uses. Of the present new media those which are characterized by a metal substrate are particularly well-suited for printing plate production, especially utilizing the low content silver, thin photosensitive layers hereinbefore described. These thin layer low silver content metal photographic media can be processed to printing plates of which the photographically produced metal image is adherently bonded to the metal substrate. After treatment of the produced metal image to render same receptive of ink, the plates are very durable and can be used in the printing of hundreds of thousands of copies, and often more than a million copies without plate failure due to separation of the image metal from the substrate metal.

For metal plates of the type described, aluminum substrates are preferred especially anodized aluminum. The surface in contact with the photosensitive emulsion is preferably a roughened surface, as by chemical roughening or physical roughening. The latter is preferred and is conveniently accomplished by brush-graining the surface, especially using nylon brushes to attain the desired roughening.

The so-called low silver content, thin photosensitive layer constitutes a preferred form of the invention, particularly with metal substrates for the production of printing plates, electrical components, and the like. As described in the aforesaid copending application, 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 than 0.5 micron. For general convenience, such fine particle size is obtained by using systems of high solids content, preferably at approximately 5% 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 addition of the arylmercuric compound, 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 gram per square meter can be readily attained and gives a uniform layer of about 0.5 micron. By adjustment, thinner layers, e.g. 0.2-0.3 micron 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 gram of silver per square meter.

The development of visible images when using the described thin photosensitive layers is preferably accomplished by physical development, which may include, as an initial step, the usual chemical development used in silver halide photography, e.g. hydroquinone aqueous solution at alkaline pH values.

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 monobath 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 the formation of undesired side products. Stabilized monobath physical developers are known in the art and usually include surfactants or similar such materials which pro-

long 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 effect 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. Lower pH values should be avoided because of the possible adverse effect on the surfactants which are sensitive to low 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 formation 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 labor 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.

The physical developer, irrespective of monobath, separate solutions or stabilization, can be applied to the photosensitive layers in the form 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.

When preparing printing plates from the new media of the present invention, physical development is continued until the photographic image is adherently bonded to the substrate, e.g. aluminum substrate. After producing the adherently bonded metal images, the media can be treated to produce a printing plate, e.g. by removal of the photosensitive layer binder, lacquering of the metal image or chemically treating the metal image to render it receptive of ink. The treatment of the metal image to obtain a printing plate is by art-recognized procedures.

Alternatively, when electrical components or nameplates are the desired products, the final treatment thereof is also by art-recognized procedures. For example, nameplates can be lacquered, with or without color to attain any desired aesthetic effect.

The photosensitive media of the present invention can be further modified by incorporating therein other materials which affect the photosensitive materials, e.g. sen-

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sitizing dyes, and other such materials which are commonly employed with the photosensitive material. For example, the reducing agent of the image-forming system employed can be present, as well as the metal ion of the physical developer, or alternatively, the entire physical developer system, all of which can be incorporated into the photosensitive layer or in separate layers on the substrate as is known in the art.

EXAMPLE 1

A 5% 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% PVOH solution thus prepared:

Solution A

Distilled H ₂ O	84.0
10% aq. NaCl	30.9
5% PVOH	14.0

Solution B

Distilled H ₂ O	84.0
10% aq. AgNO ₃	81.5
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% PVOH solution is added to the mixture under good agitation. Phenylmercuric acetate in methanol is then added at 3.0% by weight based on silver chloride and the agitation is continued for about 5 minutes thereafter. Subsequently, the mixture is filtered through a five micron bag to obtain an emulsion of the following characteristics:

Emulsion constants

1:2 rates of silver chloride to PVOH
10% excess chloride
4.5% 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 .05 g./m.² can readily be obtained.

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

Solution I

	Gms.
Ferrous ammonium sulfate	178.4
Ferric nitrate	132.3
Citric acid	180.0

Solution II

Distilled water	100.0
Synthrapol N	1.0
Armac 12D	1.0

Developer

Solution I	125.0
Solution II	25.0
3 N silver nitrate	6.0

¹ Bring to 1 liter with distilled water.

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A lustrous, coherent, metallic image is obtained on the film. Similar results are obtained with silver chlorobromide (80:20) film.

EXAMPLE 2

The following solutions are prepared as in Example 1:

Solutions

A

10 Distilled water	92.0
10% NaCl	30.9
5% Lemol 16-98	206.0

B

15 Distilled water	92.0
10% AgNO ₃	81.5
5% Lemol 16-98	206.0

C

20 30% Phenyl mercuric acetate	1.15
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The solutions are mixed in the following order: Solution A is added to Solution B, Solution C is added to the mixture. The mixture is stirred and filtered as in Example 1, to obtain an emulsion of the following characteristics:

Emulsion constants

1.3 silver chloride to binder
10% excess chloride
4.5% total solids
9.7 grams silver chloride per liter
1% 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 coater 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% excess silver at a total solids content of 4.4% is prepared from the following solutions:

Solution I

45 18 cc. 3 N AgNO ₃
210 cc. H ₂ O
72 gms. Lemol 16-98 (10%)

Solution II

50 3 gms. NaCl
210 cc. H ₂ O
72 gms. Lemol 16-98

Solution II is added to Solution I rapidly with stirring, phenylmercuric acetate in methanol is then added at 4.5% by weight based on silver chloride, and the mixture is then sonified for 5 minutes. The emulsion is then used to coat any desired substrate—film, paper, aluminum metal—at a coating weight of about 0.5 g./m.², i.e. at a thickness of one micron or less.

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

EXAMPLE 4

The following solutions are prepared:

Solution A

Distilled H ₂ O	ml.	85
Sodium chloride	gms.	6.67

Solution B

70 Distilled H ₂ O	ml.	250
Silver nitrate	gms.	15
K & K inert gelatin	gms.	20
75 Formaldehyde (3%)	gm.	1

Solution A is poured into Solution B at 60° C., phenylmercuric acetate in methanol is then added at 3.0% by weight based on silver chloride, and the resulting mixture 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 1 is repeated substituting a metal substrate for the paper substrate and utilizing the following physical developers:

AgNO ₃ (3 M) -----	ml. 15
Metol -----	g. 30
Citric acid -----	g. 80
Water to 1 liter.	

and then, in a physical developer solution which is 0.5 CuEDTA and 0.5 M Na₄EDTA. The resulting copper amplified image is adherently bonded to the substrate.

EXAMPLE 6

The procedure of Example 1 is repeated with the added step of chemical development by immersion in a standard developer, e.g. Kodak D-19 or D-76, prior to physical development, and the resulting image is of greater detail than that obtained in Example 1.

EXAMPLE 7

The procedure of Example 6 is repeated with the exception that the physical developer is the following solution:

	Ml.
CuSO ₄ (1 M) -----	50
Triethanolamine (0.75 M) -----	50
Ascorbic acid (1 M) -----	50

Comparable results are obtained.

EXAMPLE 8

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

AgNO ₃ (3 M) -----	ml. 15
Metol -----	g. 30
Citric acid -----	g. 80
Water to 1 liter.	

Comparable results are obtained.

EXAMPLE 9

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. CuSO₄/H₂SO₄ solution at coating electrical current.

The metal printed circuit is adherently bonded to the substrate.

EXAMPLE 10

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%) 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 11

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% 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 cc. of isopropanol, 144 g. of N-vinylpyrrolidone, 108 g. of n-butyl acrylate, 830 g. of N-tert-butylacrylamide and 2520 g. of vinylidene chloride. The mixture is stirred and brought to dissolution by gentle heating.

Through the dropping funnel a solution is added of 21.6 g. of ammonium persulphate in 400 cc. 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 1200 cc. 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 cc. 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-vinylpyrrolidone (70:23:3:4), the latex formed is poured into a mixture of 40 liters of 10% 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 cc. of butanone and 10 cc. 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-liter autoclave are placed successively—	
Water boiled under nitrogen -----	liters. 10.2
10% aqueous solution of oleylmethyl- tauride -----	do. 0.6
10% aqueous solution of the sodium salt of heptadecyl-disulphobenzimidazole -----	do. 0.6
Azodiisobutyronitrile -----	g. 6
Butadiene -----	g. 1500
Methyl methacrylate -----	g. 1500

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

Distilled H ₂ O -----	84.0
10% aq. NaCl -----	30.9
5% gelatin -----	14.0

Solution B

Distilled H ₂ O -----	84.0
10% aq. AgNO ₃ -----	81.5
5% gelatin -----	14.0

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Solution A is added to Solution B with good agitation over a time period of approximately 5 to 10 seconds. Phenylmercuric acetate in methanol (4% by weight based on silver chloride) is next added. Then, 248 parts of a 5% 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 .05 gram 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 12

An emulsion is prepared as described above in Example 11 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 11 and is exposed and processed as described in Example 1.

EXAMPLE 13

The following dispersion is prepared:

	Gms.
TiO ₂ (20% aq. slurry) -----	1600
Gelatin (10% aqueous solution) -----	2000
Methylanethacrylate copolymer (Hydrosol-Du Pont) (30% dispersion) -----	670
H ₂ O -----	2500
Humectant (50% aqueous solution) -----	12
Wetting agent (5% aqueous solution) -----	70
Hardener -----	5
Phenylmercuric acetate (iMeOH) (30% aqueous solution) -----	60

and then coated on brush-grained, anodized aluminum plates, a dry coating of 0.5 g./m.².

Exposure and development is effected as in Example 1 to obtain an adherent metal image which is connected to a long-run printing plate.

Similar results are obtained using diazosulfonates as the photosensitive material on aluminum plates for example, as described in U.S. Pat. 3,390,988.

EXAMPLE 14

This example illustrates a typical "contrast" silver chloride medium. The following solutions are prepared:

Sol. A:
H₂O—250 mls.
NaCl—7.5 gms.
CdCl₂—0.75 gm.
KBr—3.5 gms.
Gelatin—12.5 gms.

Sol. B:
H₂O—375 mls.
AgNO₃—20 gms.

Sol. C:
Gelatin—46 gms.

(Note.—Selection of high restrained gelatin is most important for obtaining high gamma.)

Using the double jet precipitation method, Solutions A and B are simultaneously added to a mixing vessel, insuring that Sol. A is always in slight excess and that the temperature is maintained at 116° F.

Five minutes after precipitation, gelatin C is added and dissolved, then 3 mls. of a 0.05 N H₂SO₄ solution is added with 0.9 gm. phenylmercuric acetate, the temperature increased to 150° F. and held for one hour.

The emulsion is then cooled, washed and prepared for coating. As in Example 1, the coated medium is exposed and processed.

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EXAMPLE 15

This example illustrates a common silver bromolodide medium. The following solutions are prepared:

Sol. A:
H₂O—1500 gms.
KBr—146 gms.
KI—4.4 gms.
Gelatin—57.5 gms.

Sol. B:
H₂O—1760 gms.
AgNO₃—176 gms.

Sol. C:
H₂O—250 mls.
Gelatin—222 gms.

Solution B was percolated into Solution A in 45 seconds at 160° F. and ripened for 30 minutes at 160° F., then cooled to 110° F. where Solution C was added and held mixing for 20 minutes. The emulsion was then cooled to set, refrigerated 16 hours, noodled, washed and remelted to 115° F. where 100 gms. gelatin was adjusted in volume to 5,500 grams and to pH of 6.54. The above formulation is made up to 20 gms. Ag per liter of emulsion, to which is added 0.2 g./l. phenylmercuric acetate. The emulsion is then coated, exposed and developed as in Example 1.

The image contrast and image tone of the products of the foregoing examples is significantly improved over otherwise identical media lacking the phenylmercuric acetate. Inspection of the developed media shows that "harder" or, "crisper" halftones are obtained. The presence of the phenylmercuric acetate retards bridging of halftones which has heretofore been a distinct problem, especially in Graphic Arts.

What is claimed is:

1. In a photographic medium comprising a photosensitive material which upon exposure produces a physically developable image, the improvement of having intimately associated with the photosensitive material an arylmercuric compound having the formula ArHgX wherein Ar represents an aryl group and X represents one member selected from the group consisting of an acyloxy group, a halide group and a nitrate group, said arylmercuric compound being present in an amount effective in increasing the gamma of the final print produced by exposure and contact of said medium with a stabilized physical developer comprising a solution of silver ions.

2. Medium as in claim 1 wherein the photosensitive material is silver halide.

3. Medium as in claim 2 wherein the silver halide is silver chloride.

4. Medium as in claim 1 wherein the arylmercuric compound is a phenylmercuric lower alkanolate.

5. Medium as in claim 1 wherein the arylmercuric compound is phenylmercuric acetate present in a concentration of from about 0.5% up to about 15% by weight of the photosensitive material present.

6. Medium as in claim 1 wherein the arylmercuric compound is phenylmercuric halide.

7. Medium as in claim 6 wherein the phenylmercuric halide is phenylmercuric chloride.

8. Medium as in claim 1 wherein the photosensitive material is a photoconductor.

9. Medium as in claim 8 wherein the photoconductor is a compound comprising a metal and a non-metallic element of Periodic Group VI.

10. Medium as in claim 9 wherein the photoconductor is a metal oxide or metal sulfide.

11. Medium as in claim 10 wherein the photoconductor is titanium dioxide or zinc oxide or mixtures thereof.

12. In a photographic medium comprising a photosensitive layer comprising silver halide in a binder therefor, the improvement comprising an arylmercuric compound in the photosensitive layer, said arylmercuric com-

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pound having the formula ArHgX wherein Ar represents an aryl group and X represents one member selected from the group consisting of an acyloxy group, a halide group and a nitrate group and said arylmercuric compound being present in an amount effective in increasing the gamma of the final print produced by exposure and contact of said medium with a stabilized physical developer comprising a solution of silver ions.

13. Medium as in claim 12 wherein the thickness of the photosensitive layer is less than about 300 millimicrons.

14. Medium as in claim 13 wherein the silver content of the photosensitive layer is up to about 0.5 g./m.².

15. Medium as in claim 12 wherein the thickness of the photosensitive layer is less than about 100 millimicrons and the silver content thereof is about 0.05 g./m.².

16. Medium as in claim 12 wherein the arylmercuric compound is phenylmercuric acetate present in a concentration of from about 0.5% up to about 15% by weight of the photosensitive material present.

17. Medium as in claim 12 wherein the phenylmercuric halide is phenylmercuric chloride.

18. A photosensitive medium comprising on a metal substrate a photosensitive layer comprising silver halide and phenylmercuric acetate in a binder therefor, the thickness of said layer being less than about 300 millimicrons.

19. Medium as in claim 18 wherein the silver content of said layer is up to about 0.5 g./m.².

20. Medium as in claim 18 wherein the thickness of said layer is less than about 100 millimicrons.

21. Medium as in claim 18 wherein the metal substrate comprises aluminum.

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22. Medium as in claim 21 wherein the aluminum is anodized.

23. Medium as in claim 21 wherein the aluminum is anodized and the surface in contact with the photographic emulsion is a roughened surface.

24. Medium as in claim 22 wherein the surface in contact with the photographic emulsion is a brush-grained surface.

25. In a photographic medium comprising a photosensitive photoconductor layer on a support therefor, the improvement which comprises an arylmercuric compound in the photosensitive layer, said arylmercuric compound having the formula ArHgX wherein Ar represents an aryl group and X represents one member selected from the group consisting of an acyloxy group, a halide group and a nitrate group said arylmercuric compound being present in an amount effective in increasing the gamma of the final print produced by exposure and contact of said medium with a stabilized physical developer comprising a solution of silver ions.

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U.S. Cl. X.R.

96—107, 108