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3,342,606

## PHOTOGRAPHIC RESIN COMPOSITIONS

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### ABSTRACT OF THE DISCLOSURE

A photographic composition which provides latent images within a resin composition. The images can be developed and the plates can be desensitized or fixed with use of proper materials. The photographic composition basically comprises a phenolic resin and silver nitrate. However, the invention further includes a photographic composition which comprises (1) an ethylene oxide polymer having a molecular weight greater than 30,000, (2) a phenolic resin and (3) silver nitrate present in a ratio of from about 1 part to 30 to 1 part to 7 parts phenolic resin.

This application is a continuation-in-part application of application Ser. No. 337,170 filed on Jan. 13, 1964, now abandoned.

The present invention relates to novel photographic compositions and more particularly to photographic compositions which are based on a silver nitrate/polymeric resin system.

In the past photographic films have usually been based upon silver halide-gelatin emulsion systems. The basic properties of both the silver halides and the gelatin emulsion media, however impose fundamental limitations upon these systems.

The silver halides are inherently limited by the relationship between speed and resolution. That is to say increased speed, or photoresponse, is generally accompanied by a loss of resolution.

This limitation is brought about by the nature of the image itself. The image is composed of discrete crystals or "grains." When a grain absorbs sufficient light, the entire grain is developable, that is, all the silver in the grain can be reduced. The tones of the images are composed of developed grains differing somewhat in size but with tone distinction due to the concentration of developed grains and not to size. Each grain is totally developed or is completely removed by the fixing solution.

The size of the grain, on the other hand governs the "speed" of the emulsion. The larger the grain the greater the efficiency of photon capture. Thus the speed increases with grain size but the concomitant result is that resolution declines as speed increases with larger grains.

The gelatin emulsion media is limited in that it is a relatively soft material requiring hardening procedures. This material is relatively easily scratched even after hardening.

The preparation of the silver halide gelatin emulsion is highly critical and must be conducted under highly controlled conditions. The emulsions themselves are light sensitive and must be handled and stored under relatively light free conditions.

The compositions of the present invention derive their photosensitivity from silver nitrate which is not normally photoresponsive by itself in the sense that silver halides are, but which is chemically reduceable to metallic silver in the presence of any conventional developing agent.

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However, in the compositions of this invention the compositions are photosensitive. That is, when the compositions are exposed to a light image, a latent image forms which is reduceable at a much faster rate than the composition which has not been exposed to light. Accordingly, the latent image can be reduced by a suitable developing agent to form a visible image. However, the present compositions are believed to produce an image through dye formation upon development as well as reduced silver formation and is not subject to the inherent deficiencies of the silver halide systems. Additionally, the present compositions are much more easily prepared. The coating compositions exhibit little or no photoresponse until after drying, and light free conditions are therefore not required for their preparation. When these compositions have been applied to a suitable substrate and dried, they provide a hard, scratch resistant, permeable surface.

In accordance with the present invention photographic resin compositions have been found which provide latent images within a resin composition. The images can be developed and the plates can be desensitized or "fixed" with use of proper materials. These compositions basically comprise:

- (1) phenolic resin, and
- (2) silver nitrate

Various additives can be, and preferably are, added to this basic composition to enhance certain characteristics of the composition, such as "speed" or photoresponse. These additives and their effect are discussed later below.

The phenolic resin component of the compositions of the present invention are the solvent soluble or heat-fusible condensation products of a phenol with an aldehyde. Such condensation products are divided into two classes, resoles and novolaks, either of which can be used in this invention.

While these phenolic resins are in the fusible form as ingredients, it is not necessary that these resins remain fusible after they have been incorporated into the composition. In fact, it is possible for a portion or all of the phenolic resin component to be fully advanced to the cured state.

The fusible resole phenolic resins can advance upon heating to a degree of cure and polymerization to attain a completely infusible and insoluble state. In the preparation of the present compositions only those heat fusible phenolic resins which are soluble in water or organic solvents such as acetone, ethanol and the like and which are sufficiently fusible to permit admixture and association with the ethylene oxide polymers can be used. These resins include those resole phenolic resins which have not cured to a degree of insolubility as well as the novolak phenolic resins discussed below.

#### Resole resins

Resole resins are produced by the condensation of phenols and aldehydes under alkaline conditions such as in the presence of sodium carbonate, sodium acetate, sodium hydroxide, ammonium hydroxide or the like. When the condensation reaction is complete, if desired, the water and other volatile materials can be removed by distillation, and the catalyst neutralized.

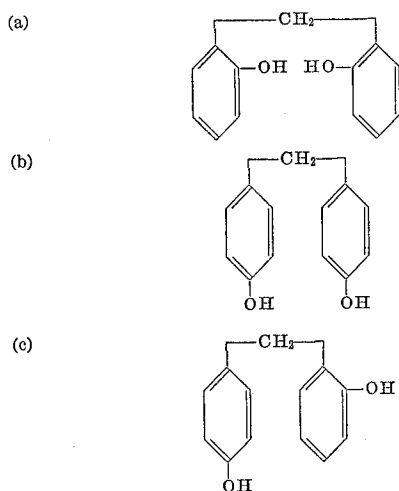
#### Novolak resins

The novolak resins are prepared in a manner similar to that used to prepare the resole resins. The distinguish-

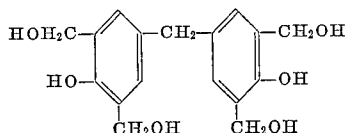
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ing exception in the preparation is that the reaction is conducted in acid media such as is obtained by use of oxalic acid, phosphoric acid and the like.

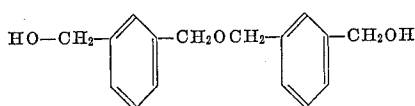
Novolak phenolic resins have different structure than the resole phenolic resins as is illustrated by the novolak condensation products of phenol with formaldehyde:



Resoles differ from novolaks in that polynuclear methylol-substituted phenols are formed as intermediates in resoles. These intermediates most likely have the structure illustrated.



The dehydrated resole may contain a preponderance of methylene ether linkages as well as some methylol groups as illustrated



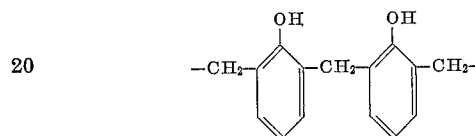
Phenolic resins are prepared by the condensation of phenol with formaldehyde or, more generally, by the reaction of a phenolic compound, having two or three reactive aromatic ring hydrogen positions, with an aldehyde or aldehyde-liberating compound capable of undergoing phenol-formaldehyde condensation. Illustrative of phenolic compounds which can be used in the preparation of the phenolic resins useful in the present compositions are cresol, xlenol, ethylphenol, butylphenol, isopropylene-ethoxyphenol, chlorophenol, resorcinol, hydroquinone, naphthol, 2,2-bis(p-hydroxyphenyl)propane, and the like. Illustrative of aldehydes which can be used in the preparation of the phenolic resins useful in the present compositions are formaldehyde, acetaldehyde, acrolein, crotonaldehyde, furfural, and the like. Illustrative of suitable aldehyde-liberating compounds which can be used to prepare phenolic resins are for example, paraformaldehyde, formalin, and 1,3,5-trioxane. Ketones such as acetone are also capable of condensing with the phenolic compounds, as are methylene engendering agents such as hexamethylenetetramine.

In a typical syntheses novolaks are prepared by heating one mole of phenol with 0.5 mole of formaldehyde

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under acidic conditions. The temperature at which the reaction is conducted is generally from about 25° C. to about 175° C. The reactants are the same as those used in the preparation of the resoles which are described and listed above. A typical syntheses of resoles involves heating one mole of phenol with 1.5 mole of formaldehyde under alkaline conditions.

While as previously stated both the resole resins and the novolak resins can be employed in the composition of the present invention, it is preferred to use the novolak resins since these produce materials of greater photosensitivity and particularly novolak resins prepared from phenols which are unoccupied in the ortho or para position to the phenolic hydroxyl. Especially preferred are the so-called "high 2,2' novolak resins". These resins contains a high percentage of compounds of the structure:



25 A more complete description of the high 2,2' novolak resins and their preparation is disclosed in U.S. Patent 2,475,587 issued to H. L. Bender et al. on July 12, 1949, entitled "Phenolic Resins" which is hereby incorporated by reference.

The silver nitrate component of the compositions of this invention is used in an optimum amount of one part to 15 parts phenolic resin. There is no clear cut lower limit of silver nitrate to phenolic resin except the amount desired to produce an image density which is desired, i.e., the less an amount of silver nitrate present the weaker will be the developed image. A ratio of one part silver nitrate to 30 parts of phenolic resin can be established as an effective lower limit.

The upper limit for the amount of silver nitrate is determined by the amount of fog or haze which is acceptable. When silver nitrate is present in an amount of about one part per seven parts of phenolic resin an objectionable fog begins to develop. While as indicated in the foregoing, there is no clear cut limitations as to the amount of silver nitrate, a desired range is from one part silver nitrate to about 10 parts phenolic to one part silver nitrate to about 20 parts of phenolic.

If the resin is not adjusted to a pH of less than 7 the resin will gradually reduce the silver in the non-image areas of the developed plate. It is therefore desirable to so adjust the composition if the plate is to be stored for any long period of time. This is conveniently accomplished through the addition of acidic additives which is discussed hereinafter.

Photographic resin systems containing only phenolic resin as the resinous component exhibit hard highly scratch-resistant surfaces but which are relatively impermeable to aqueous developing systems and accordingly, organic solvent containing development systems must be used.

As embodiment of this invention it has been found that water permeability of the plate can be provided effectively without a substantial corresponding loss in other properties by incorporating in the resin system a polar linear resin. Such resins are characterized by a relatively large number of polar groups in the molecule and are exemplified by the ethylene oxide polymers, polyvinyl alcohol, polyvinyl acetate and the like.

When such hydrophilic, polar linear resins are used it is preferred to use the ethylene oxide polymers as these resins are believed to form association products and accordingly are very compatible with the phenolic resins.

The term "ethylene oxide polymer" as used herein is intended to include ethylene oxide homopolymers as well as copolymers of ethylene oxide with other alkylene

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oxides such as propylene oxide, butylene oxide, styrene oxide and the like in minor amounts copolymerized with ethylene oxide.

Ethylene oxide polymers which can be used in the present invention are those which have molecular weights in excess of 30,000 and preferably from 50,000 to ten million.

When the hydrophilic linear polar polymer addition is used, it is generally used in an amount of from 0.1 to 2 parts per part phenolic resin and preferably from 0.5 to 1 part per part phenolic resin. The presence of these optional resins present in the preferred amounts is usually sufficient to impart water permeability to the photosensitive resin and enable development with aqueous developer.

While relatively "slow" photoresponse is sometimes desired in photographic use, "fast" photoresponse is desired for most ordinary uses. The photoresponse or "speed" of the composition of the present invention can be increased by incorporating various additives in the compositions. These additives, which can be used singly or in combination are as follows:

#### Acids

Unless acid is present the solutions of polyox, phenolic resin and silver nitrate will darken after standing for prolonged periods. It is presumed that this is due to residual basic catalyst in the polyox which causes silver oxide formation. The phenolic resin and some solvents may also contain basic components or impurities. Acidification of the solutions prevents the darkening. As indicated earlier, if the composition has a pH less than 7 the silver will not be reduced by the resin after long periods of standing.

Any acid may be used which will neither reduce nor precipitate the silver ion. Such as acid is herein defined as a compatible acid. For example, formic acid is not a compatible acid since it will reduce silver ion to silver metal. Sulfuric acid is not suitable since it will precipitate silver sulfate. A compatible acid will neither reduce silver ions to metallic silver or precipitate silver as an insoluble salt.

While acids of the organic type in general are suitable and compatible, the organic sulfonic acids have been found to appreciably increase the photosensitivity of the coatings in addition to this function of preventing darkening of the solutions. Among these acids are benzenesulfonic acid, naphthalenesulfonic acid, benzene disulfonic acid and so forth. A preferred acid is toluenesulfonic acid since it imparts very marked increase in photoresponse.

The acid additives are generally used in a neutralization amount which is usually from 0 to 0.5 part per part phenolic resin. The amount of acid necessary varies with the alkalinity of the resin components and the solvent. In this regard it should be noted that desirable compositions of this invention can be obtained by using pre-neutralized or pre-acidified resins. However, it is still preferable to use p-toluene sulfonic acid as the neutralizing acid. The pH of the composition should be less than 7.

#### Metal salts

Nickelous salts, preferably nickelous nitrate, added to the coating solution will result in developed images of greater density. It should be noted that other metallic salts which neither precipitate nor reduce the silver ion can be incorporated into the coating solution to improve the image density although their effect is less pronounced than that of the nickelous salts. The increase in image density is for practical purposes an increase in photoresponse since shorter exposures will allow development of highlight tones which otherwise are too weak to be visible. Salts of zinc, cadmium and mercury produce only marginal increases in density while cobalt and chromium salts are more effective but not as effective as nickelous salts.

The salts are used in the composition of the present

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invention in an amount of from 0.001 to 0.5 part per part of silver nitrate.

#### Halogenated alkanols

Photosensitivity can be increased by addition of proper materials which contain halogen atoms. It is presumed that reaction can occur to form silver halide. However, the reaction may be indirect, i.e. reaction with the phenolic zinc, cadmium and mercury produce only marginal increase in resin first to form halogenated phenolics which subsequently react with silver nitrate. These additives must be such that they do not react sufficiently at ordinary temperatures so as to produce a precipitate of silver halide since such precipitates cause poor coatings to form. It is believed that the additives react with the silver nitrate and/or with the phenolic resin while the coatings are drying during which time the concentration of the solutes are continually rising. These increasing concentrations as well as the higher temperatures are believed to promote the reaction.

Halogenated lower alkanols such as bromomethanol, dibromoethanol, tribromoethanol, 2-bromoethanol, 2,2-bromoethanol, 1,1,1-tribromoethanol, 2-bromopropanol, 2-chloro-3,3-dibromopropanol, 3,3,3-tribromo-2,2-dimethylpropanol, 1,1,1-tribromo-2-methyl-2-propanol and the like are suitable. The amounts of brominated alkanols used are not critical. Amounts of from 0 to 5 parts per part of silver nitrate produce satisfactory results.

1,1,1-tribromo-2-methyl-2-propanol is a particularly effective additive.

#### Iodide ion

As indicated above the halogenated alkanols increase the speed of the composition, but the presence of iodide ion is also very effective in increasing speed and also increasing photoresponse to visible light. While the presence of silver iodide in conventional systems serves to increase speed, in the present compositions it is believed that the speed increase is caused by a different mechanism than through the formation of silver iodide. The iodide ion can be used as soluble inorganic iodide such as alkali metal iodides or in the form of iodoform, ethyl iodide or other suitable material. The iodide ion donor material can be added in an amount of about one equivalent per 40 equivalents of silver ion present or in the case of iodoform about 0.05 gram per 0.5 gram of silver nitrate.

If the compositions of this invention are to be used for the preparation of X-ray plates finely divided fluorescent screen materials can be incorporated directly into the composition to enhance the response to X-ray. This technique when utilized obviates the use of auxiliary screen as is used today conventionally. Any of the materials which are fluorescent under the effect of X-ray can be used as filler materials provided they are sufficiently finely divided to be easily dispersed in the composition.

The compositions of the present invention are conveniently prepared by dissolving the ingredients in a suitable solvent. A suitable solvent is one which will dissolve the resinous components of the composition, i.e., ethylene oxide polymer when present, and phenolic resin, and the silver nitrate component. Suitable solvents include dimethylformamide, methylene dichloride and methanol in a ratio of three to one, Cellosolve and methanol or ethanol in a ratio of six to one.

Preferred as a solvent is dimethyl formamide, as this solvent dries quickly and produces excellent quality plates. It is desirable however to neutralize the dimethyl formamide with an acid, preferably with an organic acid, as discussed above relative to the resin components, since silver nitrate solution of unacidified dimethyl formamide will darken, presumably due to silver formation or silver oxide formation.

While the amount of solvent used in the preparation of the present compositions is not critical and is dependent upon the desired use of the compositions it has been found

convenient to use sufficient solvent to provide a 10 to 30 percent solution.

While the present compositions are in solution, they exhibit no photoresponse to either light or X-rays and as a result can be stored indefinitely without taking any of the precautions normally required by the conventional light sensitive silver halide compositions. If, however, halogenated alkanols are present in these compositions and it is desired to store these solutions for periods in excess of 24 hours, then it has been found desirable to store them at temperatures of about 0° C. At this reduced temperature these solutions can be stored indefinitely.

After the solutions have been prepared they can be utilized for general photographic use by coating the solutions onto a suitable substrate. The coating is applied directly from the solution by any of the conventional coating techniques known to the art. Such techniques include dipping, roller coating, knife coating, spray coating and the like. The coating is applied to the substrate to a dried coating thickness of from about 0.05 to about 0.5 mil.

Substrates which can be used to support the composition coatings include any surface which is wettable, and which is not attacked or dissolved by the solvent used. Suitable substrates include: paper; metal foil or sheet made from copper, aluminum, steel and the like; glass sheets; and plastic film and sheet made from materials such as polyethylene terephthalate polyvinyl fluoride, polytetrafluoroethylene and the like.

The selection of substrate is of course dependent upon the use to which the plate is to be used. For example if the plate is to be used as a negative or transparency then a clear substrate such as glass would be used. If the plate is desired for a use such as printing paper then a paper or metal substrate might be selected.

After the coating has been applied to the substrate, it can be dried at room temperature, i.e. 25° C. However, it has been found that the photosensitivity of the plate is greatly increased if the plates are thermally modified by drying at a temperature of from about 40° C. to about 80° C. and conveniently at about 50° C.

While the drying temperature is not critical the temperature should not exceed 100° C. as the coating can become damaged. It is important to note that while the solution of the compositions of this invention exhibit no photoresponse, the dried coating is highly photosensitive as discussed below. For this reason the drying step is conveniently effected in a light-tight oven or oven located in a dark room.

When the coated substrate hereinafter referred to as the photographic plate, has been dried it is sensitive to radiation in the range of from X-ray to ultra violet and sensitive to visible light except red and higher. For this reason red or "ruby" "safe light" can be used when handling the photographic plates.

These photographic plates can be used to great advantage in X-ray photography as well as in normal photographic uses.

When the photographic plate is used in regular photography the plate (or film roll) is mounted in a camera and exposed. The light source in such case can be sunlight, flash, photoflood or any other suitable light source. The exposure values are dependent upon the photoresponse of the plates as well as the light source, distance and so forth.

After the plate has been exposed, it is developed by immersion in a solution of an ortho or para aromatic diamine. Illustrative of the aromatic diamine developers are, p-phenylene diamine, o-phenylenediamine, o-tolidine, 4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N-( $\beta$ -hydroxyethyl) aniline.

It has been found that p-phenylene diamine gives outstanding results as a developing agent and for this reason, is preferred.

Suitable developing solvents are those which dissolve the developing agent, dissolve silver salts, and do not

attack the substrate. Illustrative of suitable developing solvents are methanol, ethanol, and a water and acetone mixture in equal parts.

The developing solution should contain from 0.1 percent to 10.0 percent of the aromatic diamine developer. A 1.0 percent solution of p-phenylene diamine has been found to give outstanding results.

The temperature of the developer solution directly affects the speed of development. The higher the temperature of the solution the more rapid the development of the plate. Reasonable development speeds can be obtained at room temperatures, i.e. about 25° C. At this temperature plates are generally developed in from 1 to 10 seconds.

It should be noted that the color of the image developed is determined by the developer used. For example, o-tolidine and p-phenylene diamine, produce a blue image; 4-amino-N,N-diethyl aniline produces a green image; and 4-amino-N-ethyl-N-( $\beta$ -hydroxyethyl) aniline produces a red-brown image.

After the plates have been developed they are desensitized or "fixed" by immersing the plates in a solution of a silver complexing agent in a suitable solvent. Illustrative of the silver complexing agents are ammonium thiocyanate, tartaric acid, thiourea and the like.

Suitable solvents for the fixing solutions are the same as those used in the developing solutions, such as ethanol, methanol and the like.

The photographic compositions of the present invention exhibit advantages hitherto unavailable in the art. These compositions are easily prepared and stored under normal lighting conditions without the necessity for elaborate precaution. The compositions are easily applied to a variety of substrates. The compositions can be easily modified to vary "exposure rating speeds" by the addition of various modifiers and additionally plates prepared from these compositions can be developed in from 1 to 10 seconds to give a permanent, apparently grainless image in a hard, scratch resistant matrix. These coating compositions can also be used to form "printing paper" normally used for "positive" prints. The image colors can be varied by the choice of developer.

The examples which follow illustrate the various embodiments of this invention. Unless otherwise indicated, all percentages given are by weight.

#### EXAMPLE I

A 5 percent solution of ethylene oxide homopolymer having a molecular weight of from 100,000 to 500,000 and a reduced viscosity of from 1.2 to 4.2 (0.2 gram in 100 milliliters of acetonitrile) was prepared in dimethyl formamide. To one-hundred milliliters of this solution was added and dissolved ten grams of a high 2,2'-novolak, phenolformaldehyde resin, one-half milliliter of concentrated nitric acid and one gram of silver nitrate. The final solution was clear and colorless.

The solution was then coated onto a 5 mil thick "Mylar" substrate, allowed to drain, and then baked in a vacuum oven at a temperature of about 70° C. After a drying period of thirty minutes the film was removed and exposed.

Development of the exposed plate was effected by immersion in a one percent solution of p-phenylene diamine in methanol. The film was fixed in a ten percent solution of ammonium thiocyanate in methanol. The film was then rinsed in methanol and air-dried. The image was dense and blue-black in color.

#### EXAMPLE II

5 percent solutions of ethylene oxide homopolymer in dimethylformamide was prepared. The ethylene oxide homopolymer had a molecular weight of from 100,000 to 500,000 and a reduced viscosity of 1.2 to 4.2 measured at a concentration of 0.2 gram in 100 milliliters of acetonitrile. This solution was divided into three 100 milliliter

aliquots. In a manner similar to that described in Example I above three different photographic compositions were prepared from these solutions; they were then coated onto a film substrate exposed and developed. The formulations of the compositions and the relative speed obtained is shown in Table I below.

TABLE I

Formulation	Formulation A	Formulation B	Formulation C
5% Poly(ethylene oxide) solution in Dimethyl formamide (ml.)	100	100	100
Phenolic Resin-Novolak high 2,2'-phenol-formaldehyde (grams)	10	10	10
p-Toluenesulfonic acid (grams)	1.5	1.5	1.5
Nickelous Nitrate (grams)	0	1.5	1.5
1-1,1,tribromo-2-methyl-2-propanol (grams)	0	0	5
Silver Nitrate (grams)	1	1	2.5
Exposure to 100 watt bulb through negative at a distance of 6 inches for a period of (seconds)	20	10	0.5

Developing Agent—p-Phenylene diamine.  
Fixing Agent—Ammonium thiocyanate.

The images produced on the photographic films of compositions A, B, and C were equivalent in all respects in spite of the fact that they were given different exposures. This clearly indicates that the nickelous nitrate and the 1,1,1-tribromo-2-propanol markedly increase the speed of these compositions.

## EXAMPLE III

Example I was repeated except that the ethylene oxide homopolymer was replaced by an ethylene oxide/propylene oxide copolymer. This copolymer contained 3 percent propylene oxide copolymerized therein. It exhibited a reduced viscosity of 7.4 measured at a concentration of 0.2 gram in 100 milliliters of acetonitrile. Plates prepared from this composition produced images equivalent to those produced by the plates of Example I.

## EXAMPLE IV

A 5 percent solution of ethylene oxide homopolymer in dimethyl formamide was prepared. The ethylene oxide homopolymer had a molecular weight of from 100,000 to 500,000 and a reduced viscosity of 1.2 to 4.2 measured at a concentration of 0.2 gram in 100 milliliters of acetonitrile. This solution was divided into three 100 milliliter aliquots. In a manner similar to that described in Example I above three different photographic compositions were prepared from these solutions; they were then coated onto a film substrate, exposed and developed. The formulations of these compositions is shown in Table II below.

TABLE II

Formulation	Formulation D	Formulation E	Formulation F
5% Poly(ethylene oxide) solution in Dimethylformamide (ml.)	100	100	100
PHENOLIC RESIN			
(1) A soluble, fusible Resole phenolic resin of phenol, and formaldehyde (grams)	10		
(2) A Novolak phenolic resin of phenol and formaldehyde (grams)		10	
(3) A high 2,2'-novolak phenolic resin of phenol and formaldehyde (grams)			10
Silver Nitrate (grams)	1.5	1.5	1.5
Nitric Acid (Concentrated) (ml.)	0.5	0.5	0.5

Photographic images were developed on each of the plates made from the compositions of D, E and F. It was estimated however that composition F containing the high 2,2' novolak resin exhibited a photoresponse about 3 times greater than composition E containing novolak resin (non-high 2,2') and that composition E exhibited a photoresponse about 10 times greater than composition

D containing the resole phenolic resin. This estimation was based upon the length of exposure required to produce equivalent images.

## EXAMPLE V

A solution of 100 milliliters of N,N-dimethylformamide, 35 grams of a grindable, high 2,2'-novolak resin prepared from phenol and formaldehyde, 4 grams of p-toluene sulfonic acid, 2.5 grams of silver nitrate and 1.5 grams of nickelous nitrate monohydrate is prepared by dissolving the solid ingredients in the N,N-dimethylformamide solvent with stirring.

This solution is coated onto a glass plate by whirl coating and is then dried in a vacuum oven at a temperature of about 50° C.

When the plate is dry it is exposed through a negative to carbon arc light source. The exposed plate is then developed by immersing in a 0.5 percent solution of p-phenylene diamine in methanol. The plate is developed immediately. After development the plate is fixed by immersion in a methanol solution of ammonium thiocyanate. A clear sharp image results.

## EXAMPLE VI

To the coating solution described in Example V above is added 0.05 gram of iodoform. The composition was coated onto a polyester resin substrate and dried in the same manner as described in Example V above.

The plate was exposed in a camera to visible light and developed as described above. The image was sharp and apparently grainless.

This image was exposed to concentrated hydrochloric acid to remove the dye image and a typical silver image was found below.

In the same manner a composition was found using a stoichiometric equivalent excess of iodoform. The composition was coated, dried, exposed and developed in the same manner. No image resulted. This indicated that the increase in photoresponse to visible light and speed is not due to the formation of silver iodide as the stoichiometric excess of iodoform insures the formation of silver iodide in the composition. While this composition could be expected to be photoresponsive, it was not under the same conditions of exposure indicating at least that the photoresponse of the composition was slower. It is therefore believed that this increase in speed is not due to silver iodide formation.

Similarly compositions were prepared identical to the above two functioning compositions wherein one part of water soluble (ethylene oxide) polymer L Polyox WSR-305 was added per six parts of phenolic resin. The compositions were coated on substrate, dried and exposed as above. The plates were developed in an aqueous 0.5 percent solution of ethylene diamine. Good sharp images resulted immediately.

What is claimed is:

1. A photographic composition comprising a phenolic resin and silver nitrate wherein the silver nitrate is present in a ratio of from about 1 part per 30 parts phenolic resin to 1 part to about 7 parts phenolic resin.

2. The photographic composition of claim 1 wherein the phenolic resin is a high 2,2'-phenolic novolak resin.

3. The photographic composition of claim 1 wherein a sufficient amount of a silver ion compatible acid is present sufficient to reduce the pH of the composition to less than 7.

4. The photographic composition of claim 3 wherein the acid is para-toluenesulfonic acid.

5. The photographic composition of claim 1 wherein from about 0.001 to 0.5 part of nickelous nitrate per part silver nitrate is present.

6. The photographic composition of claim 1 wherein iodide ion is present in an amount of from about one equivalent per 40 equivalents of silver ion.

7. A photographic composition comprising (1) an ethylene oxide polymer having a molecular weight greater than 30,000, (2) a phenolic resin and (3) silver nitrate present in a ratio of from about 1 part to 30 to 1 part to 7 parts phenolic resin.

8. A photographic plate comprising a thermally modified coating of the composition of claim 7 on a suitable substrate.

9. The composition of claim 7 wherein the phenolic resin is a high 2,2' novolak phenolic resin, and the silver nitrate is present in a ratio of from 1 part to 10 to about 1 part to 20 parts phenolic resin.

10. The composition of claim 7 wherein the ethylene oxide polymer is poly(ethylene oxide).

11. A photographic composition comprising (1) an ethylene oxide polymer having a molecular weight greater than 30,000, (2) a novolak phenolic resin, (3) from  $\frac{1}{30}$  to about  $\frac{1}{4}$  part silver nitrate per part of phenolic resin, (4) a neutralizing amount of a compatible acid, (5) from 0 to 0.5 part of nickelous nitrate per part of silver nitrate, and (6) from 0 to 5 parts of a halogenated lower alkanol per part silver nitrate.

12. A photographic plate comprising a thermally modified coating of the composition of claim 11 on a suitable substrate.

13. The composition of claim 11 wherein the halogenated lower alkanol is 1,1,1-tribromo-2-methyl-2-propanol.

14. A photographic composition comprising (1) an ethylene oxide polymer having a molecular weight of from 50,000 to ten million, (2) from 0.5 to 3.0 parts of novolak phenolic resin per part of ethylene oxide polymer, (3) from about  $\frac{1}{20}$  to about  $\frac{1}{10}$  part of silver nitrate per part phenolic resin, (4) from 0 to 0.5 part of an organic sulfonic acid per part phenolic resin, (5) from 0 to 0.5 part of nickelous nitrate per part of silver nitrate, and (6) from 0 to 5 parts of 1,1,1-tribromo-2-methyl-2-propanol per part of silver nitrate.

15. A photographic plate comprising a thermally modified coating of the composition of claim 14 on a suitable substrate.

16. The composition of claim 14 wherein the novolak phenolic resin is a high 2,2' novolak resin.

17. The composition of claim 14 wherein the ethylene oxide polymer is poly(ethylene oxide) and the organic sulfonic acid is p-toluenesulfonic acid.

18. A light stable photographic coating solution comprising (1) an ethylene oxide polymer having a molecular weight greater than 30,000, (2) a phenolic resin, (3) from about  $\frac{1}{30}$  to about  $\frac{1}{4}$  part silver nitrate per part phenolic resin and (4) a suitable solvent.

19. The coating solution of claim 14 wherein the solvent is dimethylformamide.

20. The method of preparing a photographic plate which comprises (1) preparing a solution of (a) a phenolic resin (b) from 0 to 2 parts of an ethylene oxide polymer per part of phenolic resin said polymer having a molecular weight greater than 30,000, (c) from about  $\frac{1}{20}$  to about  $\frac{1}{10}$  part silver nitrate per part phenolic resin, (d) from 0 to 0.5 part of a silver ion compatible acid per part phenolic resin, (e) from 0 to 0.5 part of nickelous nitrate per part of silver nitrate, (f) from 0 to 5 parts of a halogenated lower alkanol, per part of silver nitrate, and (g) a suitable solvent; (2) coating a suitable substrate with said solution and (3) drying said coatings at a temperature of from about 40° C. to about 80° C.

21. The method of claim 20 wherein the solvent is dimethylformamide, the phenolic resin is a novolak phenolic resin, and the acid is p-toluene sulfonic acid.

No references cited.

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