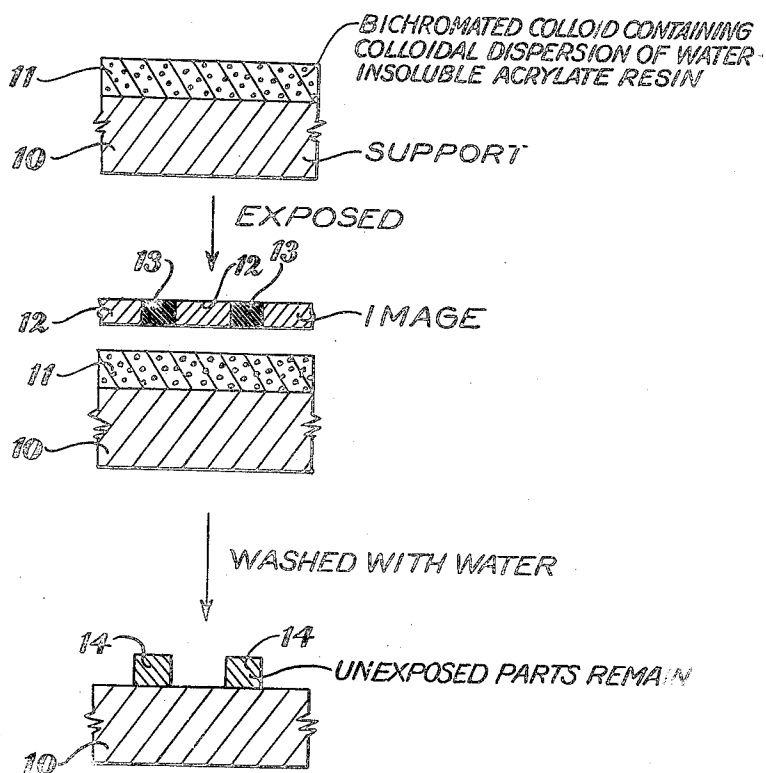


July 22, 1952

H. C. STAEHLE
PHOTOSENSITIVE COATING

2,604,388

Filed Oct. 13, 1951



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UNITED STATES PATENT OFFICE

2,604,388

PHOTOSENSITIVE COATING

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Application October 13, 1951, Serial No. 251,247
In Great Britain November 16, 1943

9 Claims. (Cl. 41—39)

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This invention relates to the preparation of photographic resist materials and to methods of forming images therefrom.

This application is a continuation-in-part of my application Serial No. 558,346, filed October 12, 1944, which is a continuation-in-part of my application Serial No. 483,339, filed April 16, 1943, both now abandoned.

The use of bichromated glue for preparing resists in the photo-engraving industry is well known and such materials have been used for many years. It is also well known that a pigment can be incorporated in the sensitized glue and a pigmented image thereby obtained. In the preparation of an image in this way, the coating of pigmented colloid must necessarily be quite thin so that exposure to light will harden the colloid throughout its entire thickness and the hardened portions will then adhere to the support upon washing with water. The unexposed portions will dissolve away. This process will yield a positive from a negative.

Reversal images may be obtained readily with gelatino-silver halide sensitive layers, but such material is relatively expensive because of the content of silver salts and cannot be easily applied and processed. The application of sensitive material containing silver salts usually requires coating and drying apparatus and the material must be processed with photographic developers and fixing agents.

I have discovered a method and means whereby it is possible to obtain a negative image from a negative, that is, a reversal image with a bichromated hydrophilic colloid, such as gelatin or glue. This material may be applied easily to most supports and may be processed simply by application of water. Its speed range is ideal for practical purposes, and it may be handled and coated in subdued daylight. Other advantages of my process and material will be evident from the following description of my invention.

The accompanying drawing illustrates my invention in flow sheet form, the figure showing sectional views of my sensitive material at various stages in the process.

My novel method for the preparation of resist materials and the production of reversal images in such materials consists in the use as a sensitive material of a bichromated hydrophilic colloid, such as, gelatin or glue, containing an aqueous colloidal dispersion of a soft synthetic resin, especially an acrylate resin, such as a polymer containing polymethyl or polyethyl acrylate. A pigment such as titanium oxide may also be included in the sensitive material. This mixture is coated on the support rather thickly, that is,

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somewhat thicker than is customary with the conventional bichromated glue and is then exposed to somewhat less light than is required for the conventional process. Upon washing with water, the exposed portions of the layer wash away completely. This action is directly opposite to that obtained with the conventional bichromated colloids. The unexposed portions may wash off in some degree but a considerable portion or all of the unexposed coating remains in contact with the support.

The essential ingredients of my sensitive composition are the bichromated hydrophilic colloid and the aqueous dispersion of a soft resin or cellulose ester. The hydrophilic colloid may be gelatin, fish glue, gum arabic, or polyvinyl alcohol. This material is sensitized with a bichromate, preferably ammonium or sodium bichromate. The resin used in the aqueous dispersion should be a soft resin and should be one which dries to a continuous film when the aqueous dispersion alone is coated on glass. Aqueous dispersions of polymethyl acrylate or polyethyl acrylate or a mixture of these are preferred. These dispersions are made by polymerizing methyl acrylate or ethyl acrylate or any mixture of the two monomers. Copolymers of methyl acrylate or ethyl acrylate with up to 25% or more of acrylonitrile are also suitable for preparing the dispersions. Aqueous colloidal dispersions of this composition are sold under the trade names Rhoplex and Acrysol. A dispersion of plasticized cellulose nitrate and water may also be employed. The mixture may also contain a wetting or dispersing agent, such as sodium alkyl sulfates, sold under the trade name Duponol C alcohol sulfates, sold under the trade names Duponol G, Duponol PC, Duponol WA, polyethylene glycols having a molecular weight above 1000, sold under the trade name Carbowax, also a plasticizing agent, such as glycerol or ethylene glycol.

When a pigment is incorporated in the sensitive material, any inert pigment may be employed. White pigments, such as titanium oxide, or lithopone may be used, or colored pigments, such as carbon black, cobalt blue, or yellow ochre. The pigment should be one which does not react with bichromates. Certain lead pigments, for example, precipitate the bichromate from the sensitive material.

As stated above, the image-forming materials of my invention may be coated on supports which are to be etched and the resist then removed or the sensitive material may be coated on a support on which it is to remain as a permanent image. The resist material may be used in the preparation of photo-engraving plates on

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copper, zinc, and anodized aluminum, in the preparation of deep etched plates for offset lithography, as a resist for preparing cellulose hydrate surfaces on films of cellulose esters and for other purposes where a highly resistant image is required. When the sensitive material is used as a resist, on metal plates the plates are preferably coated with a thin subbing layer of resin to cause the resist material to adhere more securely to the metal plate. The sensitive material is then applied and processed in the usual way. Images thus obtained may be etched with acid or alkali or a light sand blast or may be etched electrolytically. When the resist is coated on cellulose surfaces, it may be applied directly to the cellulose ester and an image formed in the usual way. The surface of the cellulose ester may then be etched by hydrolysis to form an image suitable for use in reproduction processes.

The sensitive material of my invention may be either sprayed, whirled, or brushed onto the support surface or coated by dipping, or by ordinary emulsion coating techniques, and the coating is then dried and exposed to light through a transparency and finally washed with water. The exposed areas are washed away, while the unexposed areas adhere to the support to produce the positive image. This image is quite delicate when wet but on drying becomes very durable and may be left in that form or may be protected with a lacquer coating. The final image, is, therefore, insoluble in water but is soluble in solvents for the resin of the coating, such as toluene, acetone, ethyl acetate, alcohol and ethyl Cellosolve (ethoxy ethanol), etc.

My invention will be further illustrated by reference to the accompanying drawing. As shown therein a support 10 of any suitable material is coated with a layer 11 of bichromated colloid, e. g. gelatin or glue, containing a colloidal dispersion of a water-insoluble acrylate resin. The sensitive material is exposed to light under an image having transparent portions 12 and opaque portions 13. When the exposed layer is washed with water, the portions of layer 11 which were beneath the transparent portions 12 of the image and were therefore exposed to light, are washed away leaving a relief image 14 in the portions of layer 11 which were beneath the opaque portions 13 of the image.

The following examples illustrate my invention:

EXAMPLE I

A layer capable of forming an image which withstands the action of a fine sand blast and may be used for producing fine etched designs in glass or other materials is coated from a dispersion of the following composition:

Gelatin (15% solution)	cc..	50
Acrylate resin dispersion "A"	cc..	25
Ammonium bichromate (5% solution)	cc..	5
Ammonium hydroxide	drops..	5

The gelatin used in this composition is a lime gelatin which is highly hydrolyzed during manufacture. This would be considered a very low grade of gelatin for the usual photographic processes but is entirely satisfactory for my sensitive composition.

EXAMPLE II

A composition containing a resin dispersion was prepared by first making up a mixture of 7 parts of titanium oxide in 2 parts of fish glue

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and 5 parts of water and grinding it in the ball-mill overnight. This dispersion was then added to aqueous dispersion "C" of an acrylate resin. The mixture contained the following ingredients:

5	Glue-titanium oxide dispersion	cc..	50
	Resin dispersion "C"	cc..	25
	Aqueous ammonia	cc..	1
	Sodium lauryl sulfate (20% solution)	cc..	5
10	Sodium salt of sulfonated naphthalene formaldehyde condensate (Tamol) (20% solution)	cc..	5
	Ammonium bichromate (20% solution)	cc..	2

EXAMPLE III

15 A pigmented gelatin composition was prepared from the following ingredients:

	Gelatin	grams..	60
	Water	cc..	450
20	Titanium dioxide	grams..	300
	Acrylate resin dispersion "A"	cc..	60
	Acrylate resin dispersion "B"	cc..	60
	Ammonium bichromate (5% solution)	cc..	60
	Ammonium hydroxide (28% solution)	cc..	5

25 The gelatin was soaked in ice water and when thoroughly softened was melted in hot water at about 50° C. Dry titanium oxide was added and thoroughly stirred until the mixture became reasonably smooth. At this point the acrylate resin dispersion "B" was added and the mixture passed three times through a colloid mill, after which the acrylate resin dispersion "A" was added. The mixture was cooled to room temperature and the bichromate and ammonium hydroxide then added. This mixture was refrigerated to cause it to set to a gel which melts at room temperature.

EXAMPLE IV

40 A pigmented gelatin composition was prepared from the following two mixtures:

	A. Titanium dioxide	grams..	140
	Distilled water	cc..	70
	Gelatin (15% solution)	cc..	175
45	B. Gelatin (15% solution)	cc..	175
	Acrylate resin dispersion "D"	cc..	105

50 The dry titanium dioxide was first added to water to produce a smooth slurry. To this was added slowly with vigorous stirring the gelatin solution at about 80° F. In another container half the total amount of gelatin solution was added slowly and with vigorous stirring to the acrylate resin dispersion. Part A was then added to part B with vigorous stirring and the mixture was run into a ball-mill for approximately 16 hours and was then allowed to stand for about 2 hours at 30° F. The bichromate was then added in an amount of 6 cc. of 5% ammonium bichromate solution per 100 cc. of the mixture. This mixture was found to be free flowing at a temperature of 75-80° F. At low temperatures the viscosity increases and upon keeping in a refrigerator the mixture sets to a gel.

EXAMPLE V

70 A resist material suitable for producing etched designs on glass or metals was prepared from the following ingredients:

	A. Polystyrene (25% dispersion in water)	cc..	25
	Gelatin (15% solution)	cc..	25
	B. Acrylate resin dispersion "A"	cc..	15
	Gelatin (15% solution)	cc..	25
75	C. Ammonium bichromate (5% solution)	cc..	5

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Part A was prepared by adding the gelatin rapidly to the polystyrene dispersion with vigorous stirring. Part B was made by adding the acrylate resin dispersion with vigorous stirring to the gelatin. Parts A and B were then combined and part C added.

The polystyrene dispersion was prepared by polymerization of styrene in aqueous solution in a manner similar to that described in British Patent 355,573.

EXAMPLE VI

In order to obtain black or colored images, finely divided silver halide may be incorporated in the basic mixture of gelatin, resin and bichromate. A silver halide emulsion is first prepared using low grade gelatin, such as that described in Example I. The following composition is then prepared:

Silver halide gelatin emulsion.....cc..	200
Acrylate resin dispersion "A".....cc..	90
Water.....cc..	80
Ammonium bichromate (20% solution).....cc..	6
Ammonia solution.....drops..	40

These ingredients are mixed at 110° F. and are then coated. The silver halide behaves like any other inert pigment throughout the entire process. After washing out the exposed parts of the image, the support carrying the coating is immersed in a reducing solution, such as an ordinary photographic developer whereupon the silver halide is reduced to metallic silver and a black image is thereby obtained. In order to produce colored images with this same material, the silver halide may be developed in a coupler developer. In the case of color development, the silver is then removed with Farmer's reducer.

The acrylate resin dispersions used in the above examples were prepared as follows:

The acrylates used were commercial monomers which were free of inhibitor by four short washes with one-tenth their weight of aqueous 5% sodium hydroxide, followed by four washes with water.

The acrylonitrile was distilled to remove inhibitor.

Triton 720 is a 25% aqueous solution of the sodium salt of an alkyl aryl polyether sulfonate.

The potassium persulfate and the sodium bisulfite were reagent grade chemicals.

Acrylate resin dispersion "A"

Five kg. of ethyl acrylate and 528.3 g. of acrylonitrile were mixed. In a 22 l. flask, fitted with a cork stopper, thermometer, dropping funnel, and stirrer, and surrounded by a water bath, 200 g. of Triton 720 and 33.3 g. of potassium persulfate were dissolved in 5 kg. of distilled water, and the temperature was brought to 55° C. A few pieces of solid carbon dioxide were introduced to replace the air. Stirring was begun and continued throughout the reaction. About 200 cc. of the mixed monomers was added. After about five minutes, and after every 15 minutes thereafter, and at the end, was added 25 cc. of a solution of 16.7 g. of sodium bisulfite dissolved in 200 cc. of distilled water.

About five minutes after the original addition of monomers, the contents of the flask took on a bluish-white appearance, which indicated that polymerization had started. Throughout the rest of the reaction, the mixed monomers were added continuously, with adjustment of the bath temperature to maintain a polymerization temperature of 50–60° C. Little monomer was seen

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during the reaction as it polymerized almost as fast as it was added. The reaction mixture became whiter during the reaction.

The above reaction required two hours and ten minutes, after which the contents of the flask were cooled to 30° C., filtered through cloth to remove a small amount of agglomerated material. 700 g. of Triton 720 was added to adjust the concentration of dispersing agent on a dry weight basis to 2.2% of the total weight. The pH was adjusted to 9 by the addition of 100 cc. of 1N sodium hydroxide.

The yield was 25 pounds, 3 ounces of latex containing 48.2% solids as determined by drying a sample for one day at 110° C.

Acrylate resin dispersion "B"

The above synthesis was repeated using 5528 g. of methyl acrylate as the only monomer, with the additional slight variations that 220 g. of Triton 720 was used at the end to give a detergent concentration of 1% based on the total. At this detergent level, a small amount of solid clumps were formed during adjustment of the pH to 9, and it was therefore filtered again.

This reaction took two hours, 37 minutes. The yield was 23 pounds, 14 ounces. It contained 47.3% solids.

Acrylate resin dispersion "C"

Synthesis B was repeated except that the monomers used were 2764 g. of methyl acrylate and 2764 g. of ethyl acrylate. This experiment required one hour and 28 minutes. The yield was 23 pounds, 8 ounces, containing 48.2% solids.

Acrylate resin dispersion "D"

Synthesis B was repeated except that the monomers used were 4146 grams of ethyl acrylate, and 1382 g. of acrylonitrile. This preparation required one hour, and 35 minutes. The yield was 24 pounds, containing 48.6% solids.

The sensitive dispersions prepared according to my invention may be applied to the support surface by brush application or by spraying or the support may be whirled in a manner well known in the photomechanical art. For application, the material may be diluted with water. A coating of such thickness that the surface is just covered gives best results. In the case of the titanium oxide compositions, the resulting mixture has the appearance and consistency of white or prepared paint. By varying the composition of the material, the coating thickness and the exposure, it is possible to obtain images of high contrast and excellent definition by means of my preparation. My process is particularly useful where a photographically formed image containing a minimum of organic substances is required as in the preparation of ceramic wares, reticles, photodrawings on steel, aluminum, phenolformaldehyde resin, etc. My composition adheres well to any clean surface and dries readily. Application of an air stream hastens drying.

Although my sensitive material may be applied to any clean support without the application of a subbing layer, I have found that an exceedingly thin film of some resins or cellulose esters having very slightly tacky properties greatly improves the quality of the image formed. Wiping a smooth phenol-formaldehyde resin surface with turpentine and allowing it to dry leaves a sufficient deposit of slightly tacky resin to produce a good image when my sensitive material is coated on it. Other resins such as coumarones,

alkyd resins, etc. may be used as well as plasticized cellulose nitrate, oxidized drying oils, etc. These primers seem to enhance the differentiation between the exposed and unexposed portions of the image. The unexposed coating has characteristics of the nature of resinous materials. Hence, these areas become more securely attached to the support when they are underlaid with a suitable primer. On the other hand, the exposed coating takes on many of the properties of gelatin, and since gelatin and most organic resins are relatively incompatible, the bond between the exposed coating of the support is weakened, particularly when wet, by the primer layer.

My coating composition or the material coated with it may be handled in ordinary room or shop light for a reasonable length of time without fogging the sensitive material. Upon exposure under a line drawing or photoreproduction thereof consisting of opaque lines on a clear or translucent support, a corresponding line image is produced upon washing the material with lukewarm or cool water. The material illustrated in Example II produces an image of satisfactory density and contrast upon exposure to a 150-watt mercury lamp for 15 seconds at about 10 inches. Exposure to ordinary sunlight for about the same time or less will also produce a satisfactory image. The material may, of course, be exposed for a shorter or longer time but if it is so sensitive that an exposure to high intensity light, as indicated above, for 5 seconds or less will produce an image upon development in water, the material cannot be handled freely in ordinary room illumination. I prefer, therefore, to sensitize the material so that an exposure of about 15 seconds to noon sunlight will produce an image upon development in water.

Development is carried out by immersion in or spraying with water. In most cases plain water is satisfactory although with certain compositions it may be desirable to add a hardening agent such as alum, a swelling agent such as ammonium hydroxide, or an acid such as acetic acid, or even a solvent such as alcohol. Upon development of my material the exposed portion washes off completely in the form of a delicate skin.

After exposure, development and drying, the images produced according to my invention are light stable since they consist of an inert material and are resistant to ordinary handling. They may be removed from the support by the use of abrasives or solvents for the resin but do not peel readily once they have become thoroughly dry.

As stated above, my process is distinctly different from the usual bichromated glue process in which the glue is hardened in the region of exposure. While I do not wish to limit the scope of my invention to an explanation of this phenomenon, I believe that the action of my process is somewhat as follows:

In the exposed areas there is a partial tanning of the gelatin rather than a complete tanning as in the case of the usual bichromated gelatin process. This partial tanning is accomplished with a light exposure of $\frac{1}{10}$ to $\frac{1}{20}$ of the normal exposure for other bichromate processes, even though the ratio of bichromate to gelatin is less than in prior processes. The coating in the unexposed areas behaves as though the resin had dried to a continuous film relatively unaffected by water, while the gelatin in the exposed areas reacts normally to water and dilute ammonia which causes swelling and reticulation. Thus the unexposed areas take on the properties of the resin while the exposed

areas acquire the properties of gelatin and may be washed away with water.

The image produced by this process can be hardened to form a satisfactory resist for acid, alkali, or electrolytic etching processes, for example, by heating or by treatment with a swelling agent, such as alcohol, toluene, followed by thorough drying.

Among the other advantages of my process, it affords a ready means for the preparation of templates for use in the automotive, aircraft and other industries. A metal plate from which the template is to be made can be coated with the sensitive preparation of my invention and the metal plate thus sensitized can be exposed to an image of a drawing in order to register the drawing directly upon the metal plate. My process is also useful in the layout of the actual sheet metal which is to be fabricated, as well as in making templates. My method involves the use of no organic solvents, other than minor amounts which may be employed in the precoat composition. No organic solvents are necessary in the development or processing of my material after exposure.

Where I refer in the appended claims to "reversal image" it will be understood that I mean the production of a negative image from a negative or a positive image from a positive.

Where I refer in the appended claims to exposing the sensitive coating to produce an image, it will be understood that I am using the term "image" in its broader sense to include images in photographic material such as photographic negatives or positives, as well as drawings, designs and objects themselves which may be used as patterns for the exposure.

It will also be understood that the examples and modifications described herein are illustrative only and that my invention is to be taken as limited only by the scope of the appended claims.

I claim:

1. A sensitive photographic resist material comprising a support having thereon a layer of bichromated hydrophilic colloid containing an aqueous colloidal dispersion of a water-insoluble, soft acrylate resin selected from the class consisting of polymethyl acrylate, polyethyl acrylate, methyl acrylate-ethyl acrylate copolymers, methyl acrylate-acrylonitrile copolymers containing not more than 25% acrylonitrile, ethyl acrylate-acrylonitrile copolymers containing not more than 25% acrylonitrile, mixtures of said polymers and copolymers, and mixtures of ethyl acrylate-acrylonitrile copolymers containing not more than 25% acrylonitrile and polystyrene aqueous dispersion containing not more than about 60% polystyrene dispersion, said composition being adapted to produce a light-sensitive coating in which a reversal image can be formed upon exposure to light and development in an aqueous solution.

2. A light-sensitive coating composition comprising a mixture of a bichromated glue, an aqueous colloidal dispersion of a water-insoluble, soft acrylate resin selected from the class consisting of polymethyl acrylate, polyethyl acrylate, methyl acrylate-ethyl acrylate copolymers, methyl acrylate-acrylonitrile copolymers containing not more than 25% acrylonitrile, ethyl acrylate-acrylonitrile copolymers containing not more than 25% acrylonitrile, mixtures of said polymers and copolymers, and mixtures of ethyl acrylate-acrylonitrile copolymers contain-

ing not more than 25% acrylonitrile and polystyrene aqueous dispersion containing not more than about 60% polystyrene dispersion, and a white pigment, said composition being adapted to produce a light-sensitive coating in which a reversal image can be formed by exposure to light and development in an aqueous medium.

3. A light-sensitive coating composition comprising a mixture of a bichromated gelatin and an aqueous colloidal dispersion of an acrylate resin selected from the class consisting of polymethyl acrylate and polyethyl acrylate and mixtures and copolymers thereof, said composition being adapted to produce a light-sensitive coating in which a reversal image can be formed by exposure to light and development in an aqueous solution.

4. A light-sensitive coating composition comprising a mixture of a bichromated glue, an aqueous colloidal dispersion of a water-insoluble, soft copolymer of methyl acrylate and ethyl acrylate capable of drying to a continuous film when the dispersion alone is coated on glass, and titanium oxide, said composition being adapted to produce a light-sensitive coating in which a reversal image can be formed by exposure to light and development in water.

5. A light-sensitive coating composition comprising a mixture of a bichromated glue, an aqueous colloidal dispersion of a water-insoluble, soft copolymer of ethyl acrylate and acrylonitrile containing not more than 25% acrylonitrile capable of drying to a continuous film when the dispersion alone is coated on glass, and titanium oxide, said composition being adapted to produce a light-sensitive coating in which a reversal image can be formed by exposure to light and development in water.

6. The method of making a photographic relief image which comprises coating a support with a mixture of a bichromated hydrophilic colloid and an aqueous colloidal dispersion of a water insoluble soft acrylate resin selected from the class consisting of polymethyl acrylate, polyethyl acrylate, methyl acrylate-ethyl acrylate copolymers, methyl acrylate-acrylonitrile copolymers containing not more than 25% acrylonitrile, ethyl acrylate-acrylonitrile copolymers containing not more than 25% acrylonitrile, mixtures of said polymers and copolymers, and mixtures of ethyl acrylate-acrylonitrile copolymers containing not more than 25% acrylonitrile and polystyrene aqueous dispersion containing not more than about 60% polystyrene dispersion, drying said coating, exposing it to an image, and washing away the exposed portions

of said coating with an aqueous solution to leave said coating in the unexposed portions.

7. The method of producing a photographic reversal image which comprises coating a support with a mixture of a bichromated hydrophilic colloid, an aqueous colloidal dispersion of a water-insoluble soft copolymer of methyl acrylate and ethyl acrylate capable of drying to a continuous film when the dispersion alone is coated on glass, and a white pigment, drying said coating, exposing said coating to an image, and washing away the exposed portions of said coating with an aqueous medium to leave said coating in the unexposed portions.

8. The method of producing a photographic reversal image which comprises coating a support with a mixture of a bichromated glue, an aqueous colloidal dispersion of a water-insoluble, soft copolymer of ethyl acrylate and acrylonitrile containing not more than 25% acrylonitrile capable of drying to a continuous film when the dispersion alone is coated on glass, and a white, opaque pigment, drying said coating, exposing said coating to an image, and washing away the exposed portions of said coating with an aqueous medium to leave said coating in the unexposed portions.

9. The method of making a photographic relief image which comprises coating a support with a mixture of a bichromated hydrophilic colloid and an aqueous colloidal dispersion of a mixture of a copolymer of ethyl acrylate and acrylonitrile containing not more than 25% acrylonitrile and polystyrene, said mixture containing not more than about 60% polystyrene dispersion, drying said coating, exposing it to an image, washing away the exposed portions of said coating with an aqueous solution to leave said coating in the unexposed portions and sand blasting said coating to obtain a water-receptive image in the exposed portions of said support.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,981,102	Hagedorn	Nov. 20, 1934
2,184,310	Meigs	Dec. 26, 1939
2,313,848	Toland	Mar. 16, 1943

FOREIGN PATENTS

Number	Country	Date
458,421	Great Britain	Dec. 18, 1936