Oct. 11, 1949. W. H. GRIGGS 2,484,451

BICHROMATE SENSITIZED PHOTOGRAPHIC MATERIAL

Filed July 9, 1948

FIG. 1.

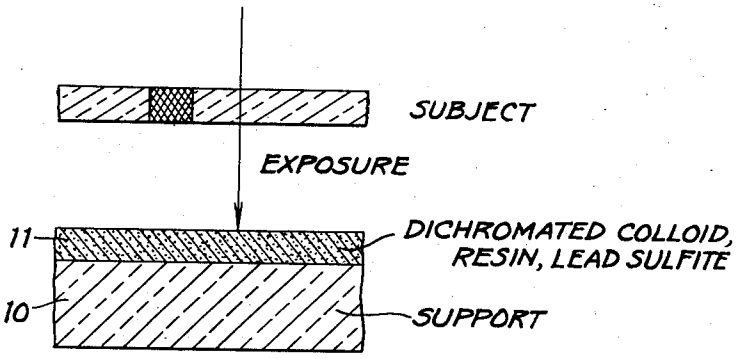


FIG. 2.

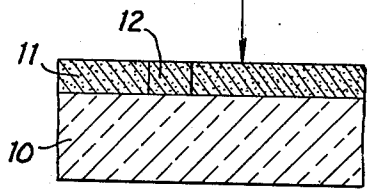


FIG. 3.

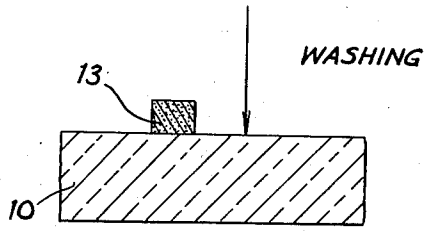
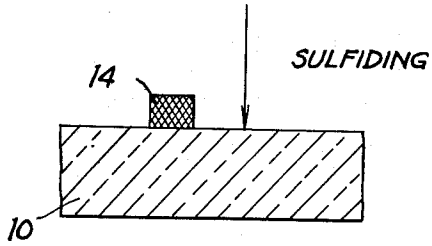


FIG. 4.



WILLIAM H. GRIGGS
INVENTOR

BY Newton M. Perrine
Wm McDowell
ATTORNEY & AGENT

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BICHROMATE SENSITIZED PHOTOGRAPHIC MATERIAL

William H. Griggs, Rochester, N. Y., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

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18 Claims. (Cl. 95—7)

1

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

In the Staehle co-pending application, Ser. No. 558,346, filed October 12, 1944, is described a process of forming positive relief images, whereby a coating of a mixture of a dichromated hydrophilic colloid and a soft, water-insoluble resin, after exposure to light, is removable in the regions of exposure by simply washing with water or alkaline solutions. The resulting resist if produced on metal, glass or similar surfaces serves as a sand-blast resist or electroplating resist. Also when black or colored pigments or dyes are incorporated or developed in the sensitive composition, the resultant relief images may be utilized as transparencies or reflection prints depending upon whether the support is transparent or opaque. One method of producing black relief images described in the above application includes incorporating carbon particles into the sensitive composition. One disadvantage of such procedure lies in the fact that the black pigment absorbs so much light that it acts as a light filter and prevents the exposure of the light sensitive material. A composition containing white or transparent pigments of course has little or no effect on the exposure as compared to the non-pigmented material.

I have discovered a colorless component for the dichromated hydrophilic colloid-resin system which effectively increases the speed of the sensitive element and which may be used to produce black direct positive relief images.

One object of my invention is to provide a photographic element of high sensitivity to light. Another object is to provide a method of producing black direct positive relief images from the compositions of my invention. A further object is to provide sensitive compositions having diverse uses. Other objects will become apparent from the following description.

The objects of my invention are accomplished in part by incorporating lead sulfite in an aqueous mixture of bichromated hydrophilic colloid, such as gelatin, and an aqueous colloidal dispersion of a soft, water-insoluble polymerized material such as a polyacrylate resin. Other objects are accomplished by processing the sensitive material to direct positive relief images, and if desired, transforming the relief image to a black image.

The accompanying drawings Figs. 1–4 show in enlarged cross-sectional view the appearance of a sensitive element of my invention during the process of exposing it to a subject, forming a direct

2

positive relief image and transforming the relief image to a black relief image.

As has been mentioned one novel feature of my invention includes using lead sulfite as a means of forming black sulfide relief images. According to the co-pending Staehle applications Ser. Nos. 558,346, filed October 12, 1944 and 745,737, filed May 3, 1947, now Patent No. 2,472,128, June 7, 1949, the use of pigments containing lead should be avoided because they destroy the sensitivity of the bichromated composition. Contrary to this I have made the discovery that one lead salt, lead sulfite, is unique in that it does not destroy the light-sensitivity of the emulsions and since it is light in color it effectively increases the sensitivity of the emulsions compared to emulsions of the type containing colored materials. It is not understood to what the unique passive property of lead sulfite should be attributed. Solubility considerations do not explain the effect because other relatively insoluble lead salts such as lead silicate, lead carbonate and lead oxalate have a deleterious effect upon sensitivity.

The sensitive compositions of my invention, are prepared and used for making direct positive relief images substantially as is described in the above co-pending patent applications as will be understood by consideration of the following examples in reference to the accompanying drawings.

Example 1

A mixture of 105 gms. lead sulfite, 2.5 grams sodium hexametaphosphate and 52 cc. water is ball-milled for 24 hours. 35 gms. gelatin dissolved in 105 cc. water is added to 140 cc. of an aqueous 25% colloidal dispersion of acrylate resin. The gelatin-resin mixture is then added to the ball mill. The resin is a copolymer containing about 90% polyethylacrylate and 10% polyacrylonitrile. Ball-milling is continued for 24 hours and then 25 cc. of 20% ammonium dichromate solution is added. After further milling the emulsion is filtered and coated to the extent of about 4 grams of solids per square foot on a suitable support such as a film, glass or metal support. Supports having a surface such as of cellulose acetate, cellulose acetate butyrate, cellulose nitrate, polyvinyl acetals, and polyacrylate resins or mixtures thereof, are especially good.

Example 2

In the above example the coating composition contained gelatin and resin in the ratio of 1 to 1.

Another suitable ratio of materials includes increasing the gelatin to a ratio of 1.5 parts per part solid resin. This is obtained by substituting in the above example 42 grams gelatin dissolved in 126 cc. water and using 126 cc. of 25% resin dispersion and compounding and coating the ball-milled mixture as described.

Example 3

When the gelatin/resin ratio is increased substantially beyond 2 to 1 the emulsion tends to become too water-soluble and the resultant relief may turn out to be a negative—rather than a positive. However, a ratio of about 2 to 1 is satisfactory and an emulsion of this range is obtained by substituting in Example 1, 52 grams gelatin in 157 cc. water and using 104 cc. of 25% resin dispersion and ball-milling and coating the emulsion as before.

I have mentioned that no more than substantially two parts gelatin per part resin is used to obtain the desired results. On the other hand, the best results are obtainable by using a minor proportion of gelatin of no less than about 0.5 part per part resin. When the gelatin is decreased appreciably more the emulsion assumes more the character of the resin, decreasing in sensitivity and the positive relief image is difficult to obtain. The preferred ratio is about 1.25 parts gelatin per part resin. It is apparent that the range of ratios and the preferred ratio may vary somewhat with choice of the type of resin dispersion, the support or gelatin or other hydrophilic colloid in use but generally the range of from 2/1 to 0.5/1 is suitable for use in most hydrophilic colloid-resin dispersions. If the proper choice of ratio of hydrophilic colloid to resin has been made, the composition may be said to be adapted to produicng direct positive relief images as above described.

The above compositions are very stable and particularly by virtue of the use of the lead sulfite component can be compounded some time prior to actual usage, that is, prior to coating on a support. As mentioned, a variety of supports may be coated or sprayed with the emulsions. A number of supports having cellulose ester or resin surfaces, preferably plasticized, such as cellulose nitrate containing dibutyl phthalate; ethyl cellulose—pure phenolic resin mixtures containing tricresyl phosphate or if desired chlorinated diphenyl resin, or a surface of a mixture of ethyl cellulose, polyvinyl acetal resin and chlorinated diphenyl resin are especially suitable. These plasticized materials are especially useful for priming any surface capable of being lacquered such as metal, wood, glass, rubber, concrete or other refractory materials. Supports such as cellulose acetate or acetate butyrate, polyvinyl butyral resin and polyacrylic ester resins generally require no priming prior to coating with my sensitive emulsions. Phenol-formaldehyde resin surfaces are generally too hard to sensitize without use of a priming coat. Similarly the adhesion of the emulsion to rubber is not good.

The bichromate sensitized elements of my invention are exposed under a 35 amp. carbon arc lamp at 18 inches for about 2–4 minutes as is shown in Fig. 1 of the accompanying drawings, wherein the emulsion layer 11 of a mixture of dichromated hydrophilic colloid, resin and lead sulfite on a transparent support 10 of, for example, polyvinyl acetal or polyacrylic ester resin, is shown being exposed to a subject containing an opaque image. As illustrated in Fig. 2, the exposure is without effect in region 12 of layer 11 but the balance of layer 11 has been hardened by exposure and the adhesion to the support so affected that when the element is subsequently treated with water or aqueous solutions containing alkali such as ammonia, sodium carbonate or an organic amine as triethanolamine, the exposed area of the layer breaks away from the support leaving the relief image 13 on support 10 as shown in Fig. 3. The element is then treated with a sulphiding agent such as 2–5% sodium sulfide solution which may contain trisodium phosphate, or treating with hydrogen sulfide solution or gas. The result is to transform the lead sulfite in image 13 to lead sulfide leaving an opaque black colloid relief image 14 of high density on support 10 as shown in Fig. 4. To obtain suitable density in image 14 the coating compositions should contain about 25–40% lead sulfite based on the total weight of solids in the emulsion. It has been found that a blacker image is obtainable by forming lead sulfite from lead sulfite as above described than by incorporating lead sulfide into the original coating composition, and of course any colored pigment originally present increases the amount of exposure required. I have found that my emulsions require as little as 1/25 as much exposure as similar emulsions containing a black pigment like carbon for obtaining black relief images.

The resin compound of my emulsions compounded as in the above examples may not only be an acrylate copolymer but acrylic ester and other resins forming aqueous colloidal dispersions are suitable such as polymethyl or polyethyl acrylate, polymethylmethacrylate, as well as polyvinylidene chloride, polystyrene, polyvinyl acetate or natural and synthetic neoprene rubber latex, the natural rubber being preferred to the synthetic. Other desirable characteristics of the resin are that it be soft, that is, aqueous dispersions of the resin do not dry to very hard films. This property can be controlled in part in a well-known manner by regulatig the degree of polymerization of the resin. The resin must also be water-insoluble and an aqueous colloidal dispersion alone must be capable of drying to a continuous film on glass.

The hydrophilic colloid used in my sensitive compositions is preferably a limed or partially hydrolyzed gelatin characterized by low viscosity and jelly strength, or gum arabic, polyvinyl alcohol and the like. It is to be understood that the term "gelatin" as used herein and in the appended claims includes ordinary gelatins or glues obtained from animal sources as well as gelatin of fish origin such as ordinary fish glues.

My sensitive compositions, in addition to having all the uses and advantages pointed out herein and in the above copending applications, are particularly useful in processes of decorating ceramic materials such as described in the application Ser. No. 745,737. The fluxing action of lead salts in glazing operations is well known, and when I produced relief designs on ceramic ware by means of the sensitive compositions containing lead sulfite, the presence of the lead salt in the relief design materially aids in the subsequent glazing steps. Lead sulfite compositions of my invention therefore serve a dual purpose in providing on the one hand black images and also providing a glazing flux.

It will be understood that my invention is to be

taken as limited only by the scope of the appended claims.

What I claim is:

1. A light-sensitive coating composition comprising a mixture of a bichromated hydrophilic colloid, lead sulfite, and an aqueous colloidal dispersion of a water-insoluble soft polymerized material selected from the group consisting of natural and synthetic rubbers, polyvinylidene chloride, polystyrene, polyvinyl acetate and polyacrylates, said composition being adapted to produce a light-sensitive coating in which a direct positive relief image can be formed by exposure to light and development in aqueous solution.

2. A light-sensitive coating composition comprising a mixture of a bichromated hydrophilic colloid, lead sulfite and an aqueous colloidal dispersion of a soft, water-insoluble polyacrylate resin, said composition being adapted to produce a light-sensitive coating in which a direct positive relief image can be formed by exposure to light and development in aqueous solution.

3. A light-sensitive coating composition comprising a mixture of bichromated gelatin, lead sulfite and an aqueous colloidal dispersion of a soft, water-insoluble polyacrylate resin, said composition being adapted to produce a light-sensitive coating in which a direct positive relief image can be formed by exposure to light and development in aqueous solution.

4. A light-sensitive coating composition comprising a mixture of bichromated gelatin, lead sulfite and an aqueous colloidal dispersion of a soft, water-insoluble polyacrylate resin, the relative amount of gelatin and resin present in said composition being of the order of from 0.5 to 2 parts gelatin per part resin.

5. A light-sensitive coating composition comprising a mixture of a bichromated hydrophilic colloid, lead sulfite, and an aqueous colloidal dispersion of a water-insoluble soft polymerized material selected from the group consisting of natural and synthetic rubbers, polyvinylidene chloride, polystyrene, polyvinyl acetate and polyacrylates, the relative amount of gelatin and polymerized material present in said composition being of the order of from 0.5 to 2 parts gelatin per part polymeric material, said composition being adapted to produce a light-sensitive coating in which a positive reversal relief image can be formed by exposure to light and development in aqueous solution.

6. A light-sensitive coating composition comprising a mixture of a bichromated hydrophilic colloid, lead sulfite and a rubber latex, said composition being adapted to produce a light-sensitive coating in which a direct positive relief image can be formed by exposure to light and development in aqueous solution.

7. A light-sensitive coating composition comprising a mixture of bichromated gelatin, lead sulfite and natural rubber latex, said composition being adapted to produce a light-sensitive coating in which a direct positive relief image can be formed by exposure to light and development in aqueous solution.

8. A light-sensitive coating composition comprising a mixture of a bichromated hydrophilic colloid, lead sulfite and an aqueous colloidal dispersion of a soft, water-insoluble polyvinyl acetate resin, said composition being adapted to produce a light-sensitive coating in which a direct positive relief image can be formed by exposure to light and development in aqueous solution.

9. A light-sensitive coating composition comprising a mixture of bichromated gelatin, lead sulfite and an aqueous colloidal dispersion of a soft, water-insoluble polyvinyl acetate resin, said composition being adapted to produce a light-sensitive coating in which a direct positive relief image can be formed by exposure to light and development in aqueous solution.

10. A light-sensitive photographic element comprising a support having thereon a layer of a mixture of a bichromated hydrophilic colloid, lead sulfite and a water-insoluble soft polymerized material selected from the group consisting of natural and synthetic rubbers, polyvinylidene chloride, polystyrene, polyvinyl acetate and polyacrylates, drying said coating, exposing said coating to an image, and washing away only the exposed areas of said coating.

11. A light-sensitive photographic element comprising a support having thereon a layer of a mixture of a bichromated hydrophilic colloid, lead sulfite and a soft, water-insoluble polymerized material selected from the group consisting of natural and synthetic rubbers, polyvinylidene chloride, polystyrene, polyvinyl acetate and polyacrylates, the relative amount of gelatin and polymerized material present in said composition being of the order of from 0.5 to 2 parts gelatin per part polymeric material.

12. A light-sensitive photographic element comprising a support having thereon a layer of a mixture of a bichromated hydrophilic colloid, lead sulfite and a soft, water-insoluble acrylate resin, said element being adapted to produce a direct positive relief image upon exposure to light and development in aqueous solution.

13. A light-sensitive photographic element comprising a support having thereon a layer of a mixture of bichromated gelatin, lead sulfite and a soft, water-insoluble acrylate resin, said element being adapted to produce a direct positive relief image upon exposure to light and development in aqueous solution.

14. A light-sensitive photographic element comprising a support having thereon a layer of a mixture of bichromated gelatin, lead sulfite and a soft, water-insoluble acrylate resin, the relative amount of gelatin and resin present in said composition being of the order of from 0.5 to 2 parts gelatin per part resin.

15. The method of making a photographic direct positive relief image which comprises coating a support with a mixture of a bichromated hydrophilic colloid, lead sulfite and an aqueous colloidal dispersion of a water-insoluble, soft, polymerized material selected from the group consisting of natural and synthetic rubbers, polyvinylidene chloride, polystyrene, polyvinyl acetate and polyacrylates, drying said coating, exposing said coating to an image, and washing away only the exposed areas of said coating.

16. The method of making a photographic direct positive relief image which comprises coating a support with a mixture of a bichromated hydrophilic colloid, lead sulphite and an aqueous colloidal dispersion of a water-insoluble, soft, polymerized material selected from the group consisting of natural and synthetic rubbers, polyvinylidene chloride, polystyrene, polyvinyl acetate and polyacrylates, drying said coating, exposing said coating to an image, washing away only the exposed areas of said coating, and transforming the lead salt in the resulting relief image to lead sulfide.

17. The method of making a photographic direct positive relief image which comprises coat-

ing a support with a mixture of bichromated gelatin, lead sulfite and an aqueous colloidal dispersion of a water-insoluble soft polyacrylate resin, drying said coating, exposing said coating to an image, washing away only the exposed areas of said coating and transforming the lead salt in the relief image remaining in the unexposed areas of said coating to lead sulfide.

18. The method of making a photographic direct positive relief image which comprises coating a support with a mixture of lead sulfite, bichromated gelatin, and an aqueous colloidal dispersion of a water-insoluble, soft, polyacrylate resin, the amount of gelatin present insaid coating being of the order of from 0.5 to 2 parts gelatin per part resin, drying said coating, exposing said coating to an image, washing away only the exposed areas of said coating and transforming the lead salt in the relief image remaining in the unexposed areas of said coating to lead sulfide.

WILLIAM H. GRIGGS.

No references cited.