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LIGHT-SENSITIVE PHOTOGRAPHIC
ELEMENT

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This invention relates to photographic materials and more particularly to films of which the light-sensitive portion consists of a bichromated layer comprising an ester or mixed ester of a polybasic organic acid with cellulose.

Bichromated layers of various colloids have long been known and used for the production of photomechanical resists and for similar purposes. Gelatin, glue and shellac have been the materials most commonly employed, but all of these possess certain inherent disadvantages. As is well known, when a bichromated gelatin layer, for example, is exposed to light, the exposed portions of the gelatin are insolubilized, while the unexposed portions are unaffected and may be washed away, leaving a relief image of the object photographed. Such gelatin relief images, however, are not satisfactory for use in certain photoengraving processes employing the etching of metals by acids, on account of the permeability of gelatin to aqueous solutions of acids and other reagents used for etching. In other instances, such as certain color photographic processes where a dye or other material is employed for producing a colored image, it is frequently necessary to add to or to form in the gelatin mordanting agents, but this is disadvantageous because these added materials have a pronounced tendency to absorb light and thus to alter the hue and/or transparency of the dye image.

The principal object of the present invention is to overcome the limitations of the prior art materials above referred to and to provide a light-sensitive photographic element which can be employed both for the production of relief images and transparencies and for the production of photomechanical resists adapted for use in photoengraving processes. A still further object is to provide a light-sensitive photographic material which is adapted for use in various color photographic processes and in which the necessity for introducing mordants for holding the color in the image layer is obviated. Another object is to produce a photomechanical resist which may be used in the etching of metals by means of acids or oxidizing solutions. Other objects will appear hereinafter.

These objects are accomplished by the following invention which, in its broadest aspects, comprises the employment as the light-sensitive material of a bichromated layer comprising an ester or mixed ester of a polybasic organic acid with cellulose. I have found that these cellulose esters may be employed in substantially the same way that gelatin, shellac, and other colloidal materials

have been used in producing bichromated layers and that they are not only capable of use for all of the above-mentioned purposes for which known materials have been employed, but are also susceptible of use in a number of processes for which known materials are wholly unsuited.

In the following examples and description I have set forth several of the preferred embodiments of my invention, but it is to be understood that they are included merely for purposes of illustration and not as a limitation thereof.

As indicated above, the esters of cellulose which I have found particularly suitable for the purposes of my invention are those derived from polybasic organic acids, such as phthalic, tartaric, and citric acids and, in fact, almost any of the polybasic organic acids which will give a cellulose ester having a free carboxyl group in its molecule. Of these, I have found the mixed organic esters of cellulose, such as cellulose acetate phthalate, cellulose acetate citrate, and cellulose acetate succinate and the like are particularly desirable in producing my improved light-sensitive colloid layers. These esters may be prepared by the technique described in the co-pending application of C. J. Malm and C. R. Waring, Serial No. 380,252, filed July 22, 1929 and comprising the treatment of a partially acetylated cellulose, such, for example, as a cellulose acetate prepared as described in U. S. Patent 1,669,944 of Clarke and Malm or a partially hydrolyzed cellulose acetate, with a dicarboxylic acid anhydride, in the presence of an organic base, such as pyridine, quinoline, and other salt-forming bases of this character. As previously stated, these particular esters are distinguished by the presence of a free carboxyl group in the molecule, the presence of this group rendering them readily susceptible of conversion into water-soluble compounds by treatment of the mixed ester with appropriate hydroxides, such as those of ammonium, sodium, potassium, and the like, some of these esters in their acid form being substantially insoluble in water. Other polybasic acid esters of cellulose which are characterized by the presence of a free carboxyl group, such as cellulose phthalate, cellulose citrate and cellulose succinate, may likewise be employed.

The technique employed for producing a light-sensitive layer in accordance with my invention is fairly simple and comprises first making up a solution of the desired ester in an appropriate solvent. Cellulose acetate phthalate, for example, may be dissolved in low concentration in a mixture of equal parts by weight of acetone

and water which has been rendered ammoniacal. The sensitizing solution is prepared by dissolving a suitable alkali bichromate such as ammonium chromate, in a dilute solution of ammonia. This solution is added to the cellulose ester solution and the resulting mixture coated on a glass plate or a suitable cellulose derivative support (previously subbed or coated with a thin layer of gelatin, since the cellulose ester solution will not readily adhere to such a surface without an undercoating of gelatin or similar substance). The plate or film is dried in the usual manner. In making up the first solution I find it preferable to employ a fairly high percentage of water, in order that the bichromate may be kept in solution, and to use sufficient ammonia to keep the cellulose mixed ester in solution and prevent it from too readily setting to a gel during the coating operation.

In general, I prefer to use ammonium bichromate as the sensitizing material and an ammoniacal solution as a source of alkali, although other alkali bichromate, such as sodium and potassium bichromates, may be employed and sodium or potassium hydroxide in place of ammonia. Alkaline earth hydroxides, however, such as calcium hydroxide, or, in fact, any of the hydroxides which form insoluble bichromates or insoluble salts of the acid esters of cellulose are unsuitable for the purposes of my invention.

The plate or film prepared as generally outlined above may be exposed in the usual manner, the exposed portions being rendered insoluble by the action of light. Those portions of the light-sensitive layer which have been unaffected are then subjected to a wash-off by lightly swabbing over the surface of the plate with cotton soaked in methyl alcohol or other suitable wash-off liquid which is a solvent for the unaffected portions of the cellulose organic ester. Other suitable wash-off liquids are dilute solutions of sodium or potassium hydroxides, and ammoniacal solution of 50% water and 50% acetone, and in general any dilute alkali which forms a soluble salt of the particular ester forming the colloid layer.

When it is desired to employ the insolubilized image as a photomechanical resist, the plate after the wash-off is subjected to treatment with a dilute acid solution in order further to harden the image by converting all of the cellulose ester into the insoluble acid form.

Example 1

A photomechanical resist may be prepared as follows: a solution is made up having the following composition:

A. Cellulose acetate-phthalate	5 gms.
Acetone	50 c. c.
Water (distilled)	50 c. c.
Ammonia (28%)	5 c. c.

A sensitizing solution is prepared having the following composition:

B. Ammonium dichromate	0.5 gm.
Water	5 c. c.
Ammonia (28%)	1 c. c.

Solution B is then added to the mixed ester solution A and the resulting mixture is coated onto the surface to be etched and dried, the coating and drying being carried out in the absence of light. In general, the sensitized plate should be used as soon after preparation as practicable. Exposure can be carried out in any convenient

way, the exposed plate subjected to a wash-off by means of methyl alcohol, and then bathed in a dilute acid solution and dried. The resulting resist may be employed in any of the usual photoengraving processes for etching metals by means of an acid etching solution.

Example II

A coating solution is made up having the following composition:

Cellulose acetate citrate (12.8% acetyl, 7.3% citryl)	0.9 gm.
Distilled water	25.0 c. c.
Ammonia (28% solution)	1.0 c. c.
Ammonium dichromate (200 gm. per liter)	1.0 c. c.

The cellulose acetate citrate is completely soluble in water. 10 c. c. of the coating solution is spread on a 5"×7" subbed glass plate and dried in a warm breeze and a clear yellow coating results. A portion of the coated plate is now exposed through the glass for five minutes in contact with a negative at 12 inches from an 8 ampere cored carbon arc. A faint brown print-out image is visible. The print is washed with distilled water for about five minutes to remove excess dichromate and swell the cellulose acetate citrate in the regions of lesser exposure. The print is now washed about one minute in a solution of 1 c. c. of 28% ammonia in 100 c. c. of distilled water, which removes the unexposed ester.

The plate is dyed for about five minutes in a solution containing 0.1 gm. of basic fuchsine and 1 c. c. of glacial acetic acid in 100 c. c. of distilled water. The plate is then rinsed in distilled water to clear the highlights. A positive dyed relief image of exceptional transparency is thus obtained.

Although I have referred in the above examples to the coating of the sensitized colloid solutions of my invention on glass supports, any suitable material may be employed as the support, such as one formed of cellulose nitrate, cellulose acetate, or any of the commonly employed support materials.

In color photographic processes and, in fact, in any process where it is desired to obtain a colored image, various dyes or other coloring materials may be incorporated in the cellulose ester solution. In general, I prefer to use the so-called basic dyes for this purpose, typical examples of which are auramine O, malachite green, rhodamine B, acridine orange, methylene blue BB, and fuchsine, although I may use such acid dyes as acid magenta and tartrazine under appropriate conditions. The dye may be incorporated directly in the cellulose ester coating solution, although it is preferable to dissolve the color in an appropriate solvent and add the resulting solution to the cellulose ester material.

Certain of the sensitized colloid layers of my invention, particularly cellulose acetate phthalate, possess the outstanding advantage over gelatin and similar bichromated layers that they may be used directly as photoengraving resists due to the fact that the cellulose acid ester material, such as cellulose acetate phthalate, for example, is insoluble and relatively impermeable with respect to water or aqueous acid solutions. As is well-known, gelatin is not suitable for use in the etching of metals in the line and half-tone processes due to its permeability to aqueous solutions. The resists produced in accordance with the pres-

ent invention, on the contrary, are susceptible of such use since acid has no deleterious effect upon the cellulose ester material and, in fact, tends to render it even more insoluble and impermeable.

5 Another outstanding advantage of the cellulose esters herein described is the fact that there is no necessity for the use of mordants therewith as is frequently the case with gelatin and similar resists in order to obtain the proper mordanting or
10 anchoring of the coloring material in the colloid layer, a basic dye, for example, tending to react with the free carboxyl of the cellulose esters herein described and thereby chemically uniting with the colloid itself. It will thus be seen that a
15 resist consisting of cellulose acetate phthalate or other mixed acid ester of cellulose is highly satisfactory because of the fact that it is itself reactive with respect to the dye and there is no necessity of using mordants which, as indicated, have a tendency to absorb light and thus degrade the
20 color of the image.

The materials of the present invention are also especially adaptable for use in certain color photographic processes, and in the manufacture
25 of various types of screens comprising minute colored elements for color photography by the screen film or screen plate processes.

For the preparation of a photoengraving resist, cellulose acetate phthalate is undoubtedly the best
30 of the esters mentioned above on account of the relative impermeability of this material in its free acid form to aqueous solutions.

I have also discovered a unique property of cellulose acetate citrate. If this material is very
35 thinly coated, for example, about 3 c. c. of solution per 5"×7" plate, and allowed to stand for several days after drying and before using, a wash-off image is not obtained with the procedure herein described. Instead, a general insolubiliza-
40 tion of the layer takes place, the exposed portions tend to repel basic dyes in dilute acid solution, while the unexposed portions take them up so that a negative image is produced in printing from a negative somewhat as in the pinatype
45 process.

What I claim is:

1. A light sensitive photographic element comprising a bichromated layer composed of a cellulose organic ester having free carboxyl groups.

50 2. A light sensitive photographic element comprising a bichromated layer composed of a mixed organic ester of cellulose having free carboxyl groups.

55 3. A light sensitive photographic element comprising a bichromated layer composed of a mixed organic ester of cellulose comprising acyl groups

of a monobasic organic ester and acyl groups of a polybasic organic acid, said last mentioned acyl groups having a free carboxyl group.

4. A light sensitive photographic element comprising a bichromated layer composed of a mixed
5 organic ester of cellulose, said ester containing acetyl groups and acyl groups of a polybasic organic ester having a free carboxyl group.

5. A light sensitive photographic element comprising a bichromated layer composed of cellulose
10 acetate phthalate.

6. A light sensitive photographic element comprising a bichromated layer composed of cellulose acetate citrate.

7. A light sensitive photographic element comprising a bichromated layer composed of cellulose
15 acetate succinate.

8. A light sensitive photographic element comprising a bichromated layer composed of a cellulose organic ester having free carboxyl groups,
20 said layer comprising a basic dye chemically united to the cellulose organic ester material.

9. A light sensitive photographic element comprising a bichromated layer composed of cellulose acetate phthalate, said layer containing a
25 basic dye chemically united to the cellulose acetate phthalate layer.

10. A photographic printing plate comprising a support having thereon an image-bearing layer, the image portion of which is composed of a mixed
30 cellulose organic ester having free carboxyl groups in its molecules, said portion being insoluble in, and substantially impermeable to, water and aqueous acid solutions.

11. A photographic printing plate comprising a
35 support having thereon an image-bearing layer, the image portion of which is composed of a mixed cellulose organic ester having free carboxyl groups in its molecules, said portion being insoluble in, and substantially impermeable to,
40 water and aqueous acid solutions, and having a basic dye chemically united to the cellulose organic ester material.

12. A photoengraving resist adapted for use with strongly acid etching solutions comprising a
45 support, having a relief image thereon, said image consisting of an insolubilized, bichromated, mixed cellulose organic ester having free carboxyl groups in its molecules.

13. A photoengraving resist adapted for use
50 with strongly acid etching solutions comprising a support, having a relief image thereon, said image consisting of an insolubilized cellulose acetate phthalate.

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