UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC FILM

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5 Claims. (Cl. 95-8)

plates and more particularly to film which at the option of the user will when finished be either matte or clear.

Numerous methods of making matte film have been suggested but in all of them the film furnished by the manufacturer was either permanently clear or permanently matte.

The present invention provides a photographic 13 film or plate (both of which are hereinafter included for convenience in the expression "film") to which a matte appearance may be imparted or not, at will, during the treatment to which the film is subjected after exposure. For this pur-15 pose, the matte appearance is produced by reaction between a substance or substances incorporated in the film and one or more ingredients of a bath or baths used in the after-treatment, such as the developing or fixing bath.

In the preferred form of the invention, the film contains a soluble salt of an alkaline earth metal, preferably calcium. Such salt is preferably incorporated in a gelatine layer applied to the back of the film, but incorporation of the salt, or of a 25 part of it, in the emulsion layer is not excluded; in the case of films coated on both sides with sensitive emulsion, such as films intended for X-ray photography, the salt may be incorporated in either or both of the sensitive layers.

In the case of flexible film this backing layer would then prevent curling. It would also give a matte appearance for inspection of the photograph and would have a rough surface for purposes of retouching or for working up the photo-35 graph. It could also be a carrier for a temporary anti-halation dye. It could also in the case of motion picture film constitute an anti-static layer.

The salts may also be incorporated in a layer between the emulsion and the support or above 40 the emulsion.

In the preferred form of the invention a soluble salt of an alkaline earth metal, preferably calcium, is used. The backing layer is of a gelatin and may be prepared by adding the salt dissolved $_{45}$ in hot water to a 15 percent gelatin solution and then adding water to bring the gelatin content to 10 percent. The following calcium organic salts have been found particularly successful: calcium benzoate; calcium salicylate; calcium 50 glycerophosphate; calcium lactate; calcium formate, and calcium acetate. In general I have found that any calcium organic salt having a moderate solubility to be satisfactory. By this I mean of more than 1 percent and less than say 55 30 percent in water. The amount of this that Patent of the United States is:

This invention relates to photographic films and may be added may be varied within wide limits depending upon the degree of the matte effect that is desired. In general I have found that 1 percent by volume of the gelatin solution that which would result in about 10 percent by volume of the dried 60 gelatin to be satisfactory.

In the processing of the film the organic salt such as calcium benzoate is transformed in an ordinary alkaline developer containing soluble alkaline carbonate and sulfite into calcium carbon- 65 ate and sulfite which remains in suspension in the layer, giving the layer a matte or opalescent appearance. On placing this film in an ordinary fixing bath comprising sodium thiosulfate and bisulfite the opalescence will disappear and a clear 70 finished film will result.

If a matte surface is desired, the best results are obtained when the film is fixed in such an acid fixing bath containing anions of oxalic acid, preferably introduced in the form of an alkali ox- 75 alate or ammonium oxalate. In such a fixing bath, calcium originally present in the film is converted into crystals of calcium oxalate having a diameter varying from about 1μ to 10μ , and producing a matte surface which is easily marked 80 by an H or HB retouching pencil. A suitable acid fixing bath is one containing about 1 percent. of ammonium oxalate.

The film may, if desired, be submitted to a solution of the oxalate of an alkali after the de- 85 veloping bath and before the fixing bath with similar results.

It is also possible to include an oxalate in the developer but I do not find this so satisfactory for retouching purposes since the crystals thus 90 formed are extremely small. The opalescent appearance is, however, secured. A further modification of the invention would comprise the forming or inclusion of calcium carbonate in the film before exposure and development. In this 95 case it would remain unchanged by the ordinary developing bath but would be removed in the fixing bath or would be fixed in position by an oxalate bath before or combined with the fixing bath. A further advantage in the presence of 100 calcium oxalate is that, if desired, it may be removed by treating the photograph with dilute hydrochloric acid, leaving the film clear and transparent.

I contemplate as included within my inven- 105 tions all such modifications and equivalents as fall within the terms of the appended claims.

Having thus described my invention what I claim as new and desire to secure by Letters

1. A sensitive photographic element comprising a support with a colloid layer thereon, there being in the colloid layer a calcium organic salt having a solubility in water greater than 1 percent 5 and less than 30 percent.

2. A sensitive photographic element comprising a support with a permanent colloid layer thereon, there being in the colloid layer a calcium organic salt having a solubility in water 10 greater than 1 percent and less than 30 percent, and having the following properties (a) that the salt and the transformation products thereof formed in an ordinary developing bath remain in position therein (b) that the salt and transfor-15 mation products thereof formed in an ordinary developing bath are soluble in an ordinary fixing

tion products thereof formed in an ordinary developing bath are transformable into crystalline particles insoluble in an ordinary fixing bath and which render the element matte.

3. A sensitive photographic element comprising a support with a permanent colloid layer thereon, containing calcium benzoate.

4. A photographic element comprising a support, a sensitized layer on one surface and a permanent colloid layer on the other surface containing calcium benzoate.

5. A photographic element comprising a support, a sensitive colloid layer and a second colloid layer containing a calcium organic salt having a solubility in water greater than 1 per cent and less than 30 per cent.

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