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2,964,405

**PHOTOGRAPHIC PRODUCTS CONTAINING
WATER-SOLUBLE SALTS OF ETHYL CELLULOSE
CHLOROPHTHALATE**

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No Drawing. Filed Aug. 8, 1958, Ser. No. 753,885

9 Claims. (Cl. 96—113)

This invention relates to photographic products containing layers containing water-soluble ethyl cellulose chlorophthalate salts particularly layers of silver halide photographic emulsions employing non-gelatin vehicles in which water-soluble ethyl cellulose chlorophthalate salt is used as the whole or as part of the vehicle so that gelling characteristics are imparted thereto. This invention also relates to the compositions employed to provide such layers.

Ordinarily, photographic emulsions have as an essential part of the composition a dispersion or suspension of a photosensitive silver halide in a vehicle therefor, usually gelatin. However, other vehicles than gelatin have been disclosed in times past for use in silver halide emulsions, but these substitutes for gelatin have been wanting in various characteristics, particularly gelling properties and, hence, have suffered in comparison with gelatin for this purpose. Gelatin is susceptible to swelling in water or developers and therefore permits processing. Gelatin exhibits gelling properties when subjected to a lower temperature and, hence, facilitates coating operations therewith. However, gelatin does exhibit certain disadvantages; for instance, it readily absorbs moisture, especially in a humid atmosphere at elevated temperatures. Under warm moist conditions gelatin may be subject to mold growth which affects the properties of the emulsion layer in which it is present. Under conditions of low relative humidity, gelatin has been known to dry unduly and exhibit brittleness.

One object of our invention is to provide a vehicle for silver halide in photographic emulsions which is free of many of the disadvantages which characterize the use of gelatin for that purpose. Another object of our invention is to provide a vehicle for silver halide having gelling characteristics at certain temperatures. A further object of our invention is to prepare photographic emulsions using an ethyl cellulose chlorophthalate salt containing carrier for the silver halide. A still further object of our invention is to provide layers, particularly photographic emulsion layers which exhibit good resistance to mechanical pressure when immersed in photographic developers. Other objects of our invention will appear herein.

We have found that water-soluble ethyl cellulose chlorophthalate salts have excellent properties as vehicles for silver halide. We have further found that mixtures of ethyl cellulose chlorophthalate salts with certain polymeric materials have properties admirably suited for vehicles for silver halide sensitive materials in photographic emulsions. We have found that as little as 1 part of ethyl cellulose chlorophthalate per 9 parts of a normally non-gelling polymer impart satisfactory gelling properties. Larger proportions of ethyl cellulose chlorophthalate salt may, however, be employed, and excellent results are obtained using ethyl cellulose chlorophthalate as the sole vehicle for the silver halide.

The nongelling polymers which may be mixed with ethyl cellulose chlorophthalate as vehicles for silver halide

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may be termed nongelling electrically neutral polymers. Some polymers of this type which are useful in this connection are hydroxyethyl cellulose, polyvinyl pyrrolidone, polyacrylamide, water-soluble cellulose acetate, water-soluble cellulose ether, dextran, dextrin, polymethyl vinyl ether, modified casein, polyethylene oxide, guar, gum arabic, water-soluble polyamides, starch derivatives, substituted polyvinyl alcohols, and polyethylene oxide derivatives. The carrier for the silver halide employed in photographic emulsions is conveniently of the order of 3–10% by weight of the liquid composition and the amount of ethyl cellulose chlorophthalate in the form of its alkali metal or ammonium salt employed in accordance with our invention constitutes from 10% to 100% of the carrier used. By this means thermoreversible gels are obtained which set upon warming thereby facilitating the coating of the emulsion upon a support.

Ethyl cellulose chlorophthalate may be conveniently prepared by reacting ethyl cellulose with chlorophthalic anhydride in an esterification bath in which acetic acid is employed as the solvent and sodium acetate is employed as the phthalation catalyst. These ethyl cellulose chlorophthalates are used in the form of their water soluble salts in which form they are obtained particularly where, for instance, sodium acetate is employed as the catalyst in the esterification process. The alkali metal and ammonium salts thereof are particularly useful.

The following examples illustrate the usefulness of water soluble ethyl cellulose chlorophthalate salt in imparting gelling properties to polymeric compositions which may be employed either for coating out of layers themselves or as the vehicle for silver halides in photographic emulsions.

Example 1

To a 7% solution in water of hydroxyethyl cellulose containing approximately 1.5 hydroxyethyl groups per anhydroglucose unit was added a 7% solution in water of ethyl cellulose ammonium chlorophthalate containing 4.9% by weight of carboxyl and 4.1% by weight of chlorine at 40° F., in the ratio of 9 parts of the former solution to 1 part of the latter. The mixture was coated out as a layer upon a cellulose acetate film support whereupon the temperature was raised to 120° F. The coating assumed the form of a clear gel which when dried gave a clear coating.

Example 2

To 9 parts of a 7% aqueous solution, by weight, of polyvinyl alcohol containing substantially no residual acetyl was mixed with 1 part of a 7% solution of ethyl cellulose ammonium chlorophthalate as described in the preceding example, at 40° F., to form a clear solution. A thin layer of this solution was applied to a cellulose acetate film support at 40° F., following which the temperature was raised to 120° F. The layer became a clear gel. It was dried in a rapid stream of air to give a clear coating. A mixture in the ratio of 4 parts of polyvinyl alcohol solution to 1 part of ethyl cellulose chlorophthalate solution gave similar results.

Example 3

A run similar to that of Example 2 was repeated except that the polymer employed was in the form of a 7% aqueous solution of a copolymer of vinyl alcohol with vinyl acetate containing approximately 12 mole percent of vinyl acetate, the solutions being in the ratio of 9 parts of copolymer solution to 1 part of ethyl cellulose ammonium chlorophthalate solution. Gelling occurred upon raising the temperature and the coating when dried was clear and had good characteristics.

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Example 4

A run was carried out similar to that of the preceding example except that the polymer employed was in the form of a 7% solution of polyvinyl pyrrolidone. When the coating was warmed, gelling thereof occurred. Upon drying, a coating of good clarity was obtained.

Example 5

A run was carried out using as the polymer, polyacrylamide, this run being carried out in the same manner as in the preceding examples. Warming caused gelling of the coating. The coating when dried exhibited good clarity.

Example 6

A silver bromiodide emulsion was prepared which involved first obtaining a silver halide dispersion in accordance with the procedure described in Yutzy and Frame U.S. Patent No. 2,614,928. The vehicle for the dispersed silver halide was a mixture of 85 parts of a 7% solution of polyvinyl alcohol and 15 parts of a 7% solution of the ammonium salt of ethyl cellulose chlorophthalate of the type described in Example 1. The addition was such that 200 grams of the vehicle, based on solid weight, was added per mole of the silver salt. The mixing of the vehicle and the silver halide dispersion was carried out at 33° F., and the emulsion composition thus obtained was coated onto a subbed cellulose triacetate film base at 46° F. The temperature was then raised to 100° F., whereupon the emulsion composition set in a few seconds and was dried by means of a current of dry warm air directed on the layer for approximately 5 minutes. A sample of the film thus formed was exposed for 1.12 second through a step wedge to light of 3,000° K. color temperature, was developed for 5 minutes in developer D-16 and was fixed and washed. The product obtained had a speed of 1.44, a gamma value of 0.77 and a fog value of .14.

Example 7

To a 5% solution in water of water soluble cellulose acetate having an acetyl content of 16% was added a 5% solution in water of ethyl cellulose ammonium chlorophthalate at a pH of 7.5 and a temperature of about 10° C. This mixture was coated onto a film support using a doctor blade and the temperature of the coating block was raised to about 110–120° F. The mixture set sufficiently that it could be dried in a current of warm dry air without causing deformation of the coating. The dried coating was clear.

Example 8

A run similar to that of Example 7 was repeated except that the polymer employed was in the form of a 5% aqueous solution of a water soluble cellulose ether instead of the water soluble cellulose acetate. When coated out upon a film support the layer formed set upon subjecting to the 110–120° F. temperature whereby it could be dried by a current of warm dry air without deformation occurring. The dry film obtained was clear.

Example 9

Example 7 was repeated using clinical dextran instead of water soluble cellulose acetate as the polymeric material. Upon applying in the form of a layer the coating obtained set when subjected to the elevated temperature whereby it could be dried by a current of warm dry air without deformation occurring. The layer obtained was transparent.

Example 10

Example 7 was repeated using dextrin instead of water soluble cellulose acetate. The mixture gelled to a gel of good consistency when heated on the coating block and the layer formed was transparent.

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Example 11

A run like Example 7 was carried out but polymethyl vinyl ether was used instead of the water soluble cellulose acetate. In the coating operation the temperature was kept at 90° F. to avoid separation into phases. At 90° F. the coating formed set to a fairly firm gel which could be dried in a current of warm dry air to form a transparent layer. The layer was tacky which is characteristic of the polymeric ether used.

Example 12

To 8 parts of a 5% solution in water of casein which had been enzymatically degraded was added 1 part of a 5% solution of ethyl cellulose ammonium chlorophthalate at a pH of 7.5 and a temperature of about 10° C. The composition was coated out onto film base as described in Example 7. When the temperature of the coating block was raised to 110–120° F. setting was good and the coating was dried to form a transparent layer.

Example 13

Example 7 was repeated substituting a polyethylene oxide polymer for the water soluble cellulose acetate. When the mixture was heated on the coating block setting occurred. The set layer was dried in a current of warm dry air without deformation, forming a transparent layer of the polyethylene oxide polymer.

In the compositions in accordance with our invention, the presence of salts is undesirable and this includes polymers containing substantial amounts of ionizing groups such as sulfonated polystyrene, carboxymethyl cellulose and the like.

Although our invention is primarily directed to the providing of means for coating emulsion layers in the obtaining of photographic products, it will be apparent that our invention is useful in any situation where layers of polymers of significant thickness are deposited from aqueous solution, for instance, in the application of coatings for protective or decorative purposes, pigmented coatings, coatings carrying abrasives or magnetic materials, or the like.

The compositions in accordance with our invention are, of course, useful for the application of layers for photographic products. For instance, these compositions may be employed as carriers for dyes in the application of antihalation layers to photographic film.

The following example illustrates the preparation of an ethyl cellulose ammonium chlorophthalate which is useful in preparing compositions in accordance with our invention.

50 parts of an ethyl cellulose having an ethoxyl content of approximately 45% was dissolved in 250 parts of pyridine and 250 parts of acetone. There was added 76 parts of 3- and 4-chlorophthalic anhydride. The mass was refluxed for 7 hours. It was then cooled, diluted with an equal volume of acetone and precipitated into distilled water. The ethyl cellulose chlorophthalate obtained was thoroughly washed with distilled water and dried. Some of this compound was converted to the ammonium salt by suspending 30 parts of the ethyl cellulose chlorophthalate in 970 parts of distilled water, cooling on an ice bath, and adding ammonium hydroxide to the stirred solution until a clear viscous solution was obtained. A solution having a pH of 8 and a minimum viscosity at 36° F., was obtained. The solution set to a clear firm gel at 40° F.

There was added to a 3% solution of the ammonium salt of ethyl cellulose chlorophthalate as prepared above a silver halide dispersion, prepared in accordance with the method described and claimed in Yutzy and Frame Patent No. 2,614,928 and which contains no more than a negligible amount of gelatin, in sufficient amount to produce a high contrast emulsion, the temperature being held below 40° F. A layer of the emulsion was applied to a cellulose triacetate film support. The support was

then led into a chamber having a 100° F. temperature. The liquid emulsion on the support set to a firm gel and the layer was dried by means of a current of warm dry air applied thereto. The resulting dried emulsion layer remained flexible over a wide range of relative humidities, imparted very little curl to the support, was not tacky at high relative humidity, and was not attacked by micro organisms.

In the processing of photographic emulsion layers, those containing ethyl cellulose chlorophthalate salts when not provided with a hardener exhibit good resistance to mechanical pressure as compared to conventional photographic emulsion layers which have not been hardened. This softness, called "mushiness," is determined by the grams of weight of a stylus necessary to penetrate the polymer layer wet with an aqueous bath. Whereas in the case of conventional carriers for silver halide (unhardened) a pressure of only 10 to 25 g. gives penetration, a pressure of 180-200 g. has been necessary to penetrate layers of ethyl cellulose chlorophthalate salt, when the respective layers were placed in a bath of photographic developer. This eliminates the necessity of adding a hardener which sometimes introduces other properties which may be undesirable such as decrease of the rates of development and fixing.

We claim:

1. A photosensitized material comprising a support having thereon a layer of a silver halide photographic emulsion, the carrier for the silver halide of which comprises 10-100% of a water soluble salt of ethyl cellulose chlorophthalate.

2. A photographic emulsion comprising silver halide carried by a composition of which 10-100% of the total solids therein is a water soluble ethyl cellulose chlorophthalate vehicle.

3. A composition for applying layers to a support in the making of photographic materials which comprises

a mixture of water soluble nongelling electrically neutral polymer and at least 10% and less than 100% based on the total mixture of a water soluble ethyl cellulose chlorophthalate in aqueous solution.

4. A composition for applying layers to a support in the making of photographic materials which comprises a mixture of hydroxyethyl cellulose and at least 10% and less than 100% of the mixture being ethyl cellulose ammonium chlorophthalate in aqueous solution.

5. A composition for applying layers to a support in the making of photographic materials which comprises a mixture of polyvinyl alcohol and at least 10% and less than 100% of the mixture being ethyl cellulose ammonium chlorophthalate in aqueous solution.

6. A composition for applying layers to a support in the making of photographic materials which comprises a mixture of polyvinyl pyrrolidone and at least 10% and less than 100% of the mixture being ethyl cellulose ammonium chlorophthalate in aqueous solution.

7. A photographic emulsion comprising silver bromoiodide carried by a mixture of polyvinyl alcohol and at least 10% and less than 100% of the mixture being ethyl cellulose ammonium chlorophthalate.

8. A photosensitive product comprising a layer upon a cellulose triacetate film support of a photographic emulsion comprising silver halide carried by an ethyl cellulose ammonium chlorophthalate vehicle.

9. A photographic material comprising a support and a polymer layer thereon which contains 10-100% based on the total solids in the polymer layer of a water soluble salt of ethyl cellulose chlorophthalate.

References Cited in the file of this patent

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