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PHOTOGRAPHIC EMULSION COMPOSITIONS AND THEIR PREPARATION

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Our invention relates to photographic emulsions which employ ethyl cellulose phthalate as the carrier for the silver halide therein.

Since the earliest days of photography, research has been directed toward the discovery of suitable vehicles for the light-sensitive silver salts. Thus, collodion, which was originally employed for this purpose, gave way to the use of gelatin, which latter had the advantageous properties of being coatable from water solution and usable in dry form. Gelatin is susceptible to swelling in water or developers, and therefore permits processing. In view of the widely accepted use of gelatin as a silver halide vehicle at the present time, the photographic industry has associated water permeability, and therefore water sensitivity, with the emulsion layer, with the result that vehicles other than gelatin which have been proposed usually have properties similar to gelatin, particularly in being susceptible to swelling by water and to processing in aqueous solutions.

Gelatin has, however, exhibited properties which have been regarded as undesirable under certain circumstances. For instance, gelatin absorbs moisture readily when in an atmosphere having a high relative humidity, and, as a result, may thereby become soft and tacky. Also, under warm, moist conditions, gelatin is subject to the action of mold growth which has a derogatory effect upon the photographic image which may be formed by the emulsion. Gelatin, when subjected to an atmosphere of low relative humidity, loses moisture to the air and becomes dry and brittle. This loss and gain in moisture may contribute to curling of the film holding a gelatin layer due to changes in its moisture content from one time to another.

One object of our invention is to provide a vehicle for silver halide which will be free 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 in photographic emulsions in which the silver halide may be subjected to processing by developing and fixing solutions to good effect. A further object of our invention is to provide a vehicle for silver halide in photographic emulsions, the properties of which permit rapid coating of the emulsion upon the support therefor, and the use of hot air for quickly setting and drying the photographic product. A still further object of our invention is to prepare photographic emulsions using ethyl cellulose phthalate as the carrier for the silver halide therein. Other objects of our invention will appear herein.

We have found that dispersed silver halide may be carried in aqueous solutions of ethyl cellulose phthalates, and the photographic emulsions prepared therefrom are characterized by good flowability while cold, which emulsions, after coating, may be readily gelled or set by the application of heat thereto. We have found that the emulsion layers prepared using ethyl cellulose phthalate as the carrier, after exposure, are readily susceptible of processing in conventional developers and fixing solutions to give photographic products of good quality. We have also found that photographic films prepared using ethyl cellulose phthalate as the carrier for the silver halide are resistant to the effects of changing humidity conditions, and, as a result, the photographic material is not affected by organisms, nor is there any appreciable change in flexibility, nor any effect on the curling characteristics on the film which is prepared therefrom.

The ethyl cellulose phthalate which is employed is in the form of its salt, such as the ammonium salt, the amine salt (either primary, secondary or tertiary), or, in some cases, in the form of the alkali metal salts thereof. These emulsions are ordinarily prepared by mixing the ethyl cellulose phthalate salt with the silver halide after it has been prepared in a peptizer so as to be in dispersed form. In some cases it may be desirable to mix the salt of ethyl cellulose phthalate with the peptized silver halide, and immediately coat the resulting composition upon the support. In other cases it may be desirable to mix the carrier with the peptized silver halide and coat either at the time or allow standing for a certain length of time. The silver halide grains may be prepared using any commonly employed peptizer therefor, as is well known in the art. As a peptizer for the silver halide, the ethylenediamine salt of ethyl cellulose phthalate can be employed, and the emulsion may be prepared therefrom by mixing therewith as the carrier either more of the same type of salt with the silver halide dispersion so prepared or one of the other salts of ethyl cellulose phthalate. Another type of peptizer which has been found to be useful for preparing silver halide dispersions is the gelatin derivative type, such as phthalic anhydride derivatives of gelatin, as disclosed and claimed in U. S. Patent No. 2,525,753 of Yutzy and Frame, or gelatin derivatives as disclosed in U. S. Patent No. 2,614,928 of Yutzy and Frame. This peptizing material is compatible with ethyl cellulose phthalate salts and, upon mixing therewith, the resulting emulsion obtained may be allowed to remain in storage for any period desired. Other peptizers which may be employed in preparing the silver halide dispersions may be gelatin, oxidized protein derivatives or oxidized proteins as described in Lowe and Gates U. S. Patent No. 2,691,582 of October 12, 1954 or ethanol amine cellulose ester compounds. In cases where the peptizing material employed is not highly compatible with the ethyl cellulose phthalate salt, it is desirable that the coating operations take place very soon after the mixing of that carrier with the peptized silver halide dispersion.

In the coating of photographic emulsions in accordance with our invention, the emulsion is at a temperature lower than that to which the coating is subjected after it has been applied to the support therefor. For instance, the cellulose ether phthalate salts as employed in our invention are water-soluble, but insoluble in water at elevated temperatures, the solution temperature depending upon the particular cellulose ether phthalate employed. Therefore, it is preferred to dissolve the cellulose ether phthalate salt and prepare the photographic emulsion therefrom under cold conditions and, after coating, then apply a higher temperature thereto, such as by the use of hot air, which immediately sets the coating. Our method of coating emulsions is especially useful in preparing photographic papers due to the fact that setting of the emulsion layer can be accomplished so rapidly that there is little, if any, penetration of the paper by the emulsion applied thereto. Consequently, papers without any preparatory coating can be employed as the support for emulsions applied in accordance with our invention. Emulsions in accordance with our invention can be coated upon glass, cellulose ester film support, paper, resin film support or any other material which is suitable as a support for a photographic layer.

The following is an example of the behavior of a typical cellulose ether phthalate useful in our invention: An ethyl cellulose, having an ethoxyl content of approximately 45%, was phthalylated according to the method described in U. S. Patent No. 2,093,462 to give a cellulose ether phthalate having an apparent phthalyl content of 16.8%. This compound had a viscosity, when made into a 3% solution in ethyl alcohol (70%), isopropyl alcohol (20%), n-butyl alcohol (10%) of 7.4 cps. 40 grams of the dry cellulose ether phthalate was added to 960 cc. of distilled water, and the slurry formed was cooled to 40° F. Ammonium hydroxide was added drop-wise with stirring until solution was effected. The clear, filtered solution had a pH of approximately 8.0. It was found that this solution had its lowest viscosity at a temperature of 62° F. When the temperature is increased, the viscosity of the solution rises sharply, and shortly beyond 66° F. the solution sets to a firm gel. This gel can be dried in a strong current of warm air at a dry and wet bulb temperature wherein the wet bulb temperature is at least the setting temperature of the cellulose ether phthalate. For example, it may be convenient to dry the gel at 100° dry bulb and 67° wet bulb temperature. If rapid drying is desired, a dry bulb temperature of 130° F. and a wet bulb temperature of 80° F. can be employed. In the coating of gelatin solutions upon cellulose ester film base or the like, it is customary to add wetting agents to the solution to bring about an even wetting of the surface to be coated. In the case of the salts of cellulose ether phthalate, we have found that the use of any wetting agent is unnecessary, as the solutions themselves readily wet most surfaces, and the coatings formed on the film base show remarkable uniformity and freedom from blistering or other effects often met with in the coating of gelatin emulsions on film base. Also, in the use of cellulose ether phthalate as the carrier for silver halide, the addition of hardeners is unnecessary, as the vehicle in its free acid state is almost completely unaffected by water, either in the vapor or liquid form. If water of a basic character (hard water) is employed, there may be conversion of some of the vehicle to the form of a salt, which would render the vehicle more susceptible to the effect of water, particularly at low temperatures. In that case, prehardening of the vehicle may be desirable.

In the preparation of light-sensitive silver emulsions, it is customary to react silver nitrate with a halide salt, such as potassium bromide, in the presence of a colloidal material. It is often desirable to remove the excess of soluble salts present by means of washing. With a gelatin vehicle, this washing is accomplished by setting the emulsion to a gel by chilling, forming noodles thereof and washing these noodles in cold water. This method is slow and costly, and some silver and gelatin are lost in the proceeding. In the case of a cellulose ether phthalate emulsion, the noodling is accomplished by forcing a thin stream of the liquid emulsion into dilute aqueous acid, such as dilute acetic acid. The emulsion precipitates in a thread-like form which is susceptible to being washed in a stream of water of any desired temperature. The soluble salts therein are thereby removed without any loss of silver or cellulose ether phthalate. After this washing operation, the emulsion coating may be carried out by chilling the washed noodles of emulsion, adding a small amount of water containing dilute alkali, and then adjusting the resulting solution to give the correct silver content and viscosity. When the emulsion is free of bubbles, it is ready for coating.

In the coating of emulsions in accordance with our invention, there is some slight difference in behavior, depending on the base used to form the salt. For instance, where the sodium salt of the cellulose ether phthalate is used, the emulsion layer, after drying, is water permeable and remains so until contact with an acid, and because of this characteristic of the sodium salt of the cellulose ether phthalate, it is more desirable for use in preparing emulsions which are coated onto paper, the carrier of the emulsions being wholly or partly the alkali metal salt of the cellulose ether phthalate. In the case of the ammonium salt of the cellulose ether phthalate, on the other hand, the drying operation in the coating of the emulsion layer liberates the ammonia therefrom so that the free acid form of the cellulose ether phthalate is obtained. Thus, with a film base as the support, a dried film is obtained having an emulsion layer thereon which is no longer water soluble. Because of this characteristic, ordinarily the use of the ammonium salts is preferred for preparing emulsions to be used on film base. Although ethyl cellulose phthalate is soluble, as a rule, in cold water having an alkaline pH, nevertheless emulsion layers in accordance with our invention can be processed in the conventional alkaline developer solutions without any undue softening or disintegration taking place. Also, emulsion layers in accordance with our invention are not susceptible to the effect of high humidities, nor do they support the growth of mold as characterizes gelatin emulsions. In addition, the emulsion layers in accordance with our invention show a high degree of flexibility over a wide humidity range, and there is no tendency to cause curling as a result of changes of humidity conditions.

In the development of emulsions using a cellulose ether phthalate vehicle, we have found that, although this vehicle is impervious to the action of neutral and acidic solutions, this material is changed by the alkali of a developer into a water permeable material, and consequently upon development the action on the silver grains proceeds at once and the development time is the same or even less than that of the same kind of grains dispersed in gelatin. It is preferable in fixing emulsion layers according to our invention that a neutral rather than an acid hypo solution be employed for this purpose. After the desired fixing has been accomplished, the emulsion can then be immersed in aqueous acid, such as dilute aqueous acetic acid, for a minute more or less to convert the cellulose ether phthalate to the water insensitive form. The moisture content of the emulsion layer is appreciably reduced thereby, and after this treatment the film or paper containing the emulsion layer may be washed in water in normal fashion. Due to the decrease of the moisture content of the emulsion in the acid bath, the washed film is so nearly dry that it may be used for some purposes after merely blotting off the surface moisture. As a negative, contact prints may be made therefrom immediately without damage to the emulsion layer. As an X-ray film, diagnosis can be made immediately after processing without the precautions ordinarily necessary in the case of gelatin emulsions.

The temperature at which photographic emulsions exhibit minimum viscosity on one hand, and setting on the other, varies from one cellulose ether phthalate to the other. For instance, it may be stated as a generality that the higher the ethoxyl content, the lower the temperature necessary to dissolve the cellulose ether phthalate, whereas the higher the phthalyl content, the higher the temperature necessary for setting the solution of the ether phthalate and the less critical the setting temperature becomes. Also, the setting point of the cellulose ether phthalate solution will vary with the concentration thereof. For instance, with a solution of 5% concentration, the setting point of a given cellulose ether phthalate will be several degrees lower than that of a solution of 3% concentration. As a rule, it is preferred to operate near a ratio of 5:1 cellulose ether phthalate solution to concentrated silver halide dispersion when the cellulose ether phthalate is about 5% concentration in water and the concentrated silver halide contains about 2% of peptizer with 1 mol of silver halide therein per liter of solution. It is desirable that sufficient ethyl cellulose phthalate be employed as a carrier for the silver halide to obtain an emulsion coating on a support of film or paper when the emulsion is applied thereto so as to obtain a photographic product.

It is desirable that the cellulose ether phthalates employed be prepared from ethyl cellulose having an ethoxyl content of at least 42%. When a cellulose ether having an ethoxyl content of about 42% is used to prepare the cellulose ether phthalate, it is desirable that the ether phthalate contain at least 5% phthalyl, the preferred range for phthalyl content for a cellulose ether phthalate so prepared being 8–15%. When a cellulose ether having an ethoxyl content of 47.7% is used as the starting material, a phthalyl content of at least approximately 11% has been needed to get a product whose salts are soluble in cold water. We have found that the preferred range of phthalyl to impart to cellulose ethers of this type is within the range of 11–17%. When cellulose ethers having a still higher ethoxyl content, such as 49.5%, are used to prepare ether phthalates, few hydroxyl groups are present in the cellulose ether, and therefore the amount of phthalyl which can be incorporated is limited. In this case, 16.5% phthalyl is approximately the limit of phthalyl which can be incorporated, but at least approximately 12% of phthalyl should be imparted for solubility of the ether phthalate salts in cold water. The cellulose ether phthalates employed may vary also as to viscosity. We have found that in the case of low viscosity esters, such as those whose salts have a viscosity of less than 10 cps. in 4% solution in water, it is usually desirable to incorporate some plasticizer, such as triacetin or polyethylene glycol in the cellulose ether phthalate composition. In the case of higher viscosity esters, plasticizer is usually unnecessary.

In applying emulsion layers in accordance with our invention using cellulose ether phthalate, it is preferred that the layer have a thickness when dry of at least .00035 of an inch for cine positive film. With other types of photographic products, the emulsion layer has a dry thickness from .0001 to .001 inch or more. For applying on film base, it is desirable that that base be first subbed with a layer which promotes good adhesion. For instance, film base having a layer thereon of a mixture of cellulose nitrate and gelatin is useful for forming photographic products in accordance with our invention.

Instead of cellulose ether phthalate, some other dicarboxylic acid ester of the cellulose ether may be employed as the carrier for the silver halide in accordance with our invention, such as the succinate, the maleate or the like.

The following examples illustrate our invention:

Example 1

2 parts of starch acetate were dissolved in 30 parts of distilled water, warming gently. The solution was cooled to 40° F. and there was then added thereto simultaneously in slow streams and with vigorous stirring 10 parts of a silver nitrate solution and 10 parts of a solution of potassium bromide and iodide. The silver nitrate solution had been made by dissolving 100 grams of silver nitrate in 200 cc. of distilled water. The second solution had been made by dissolving 76 grams of potassium bromide and 2.4 grams of potassium iodide in 200 cc. of distilled water. The preparation of the silver halide and the remaining steps in this example were carried out under darkened conditions.

The resulting product which comprised grains of silver halide dispersed in the starch acetate solution was mixed with 50 parts of a 5% solution of the ammonium salt of ethyl cellulose phthalate, the temperatures of both solutions being at approximately 50° F. The cellulose ether phthalate employed was the result of phthalylating a cellulose ether having an ethoxyl content of 45% to a point that a phthalyl content of 19.8% was present therein. The suspension of silver grains in cellulose ether phthalate obtained was then forced through a small glass tube into dilute acetic acid, thus producing a thread-like precipitate of the acid form of the cellulose ether phthalate carrying the silver halide grams. This precipitate was washed in a stainless steel wire basket with water until the wash water which resulted no longer gave a test for soluble halides. The precipitate was then partially dried and was mixed with 100 parts of distilled water containing 1 part of starch acetate therein. The slurry thus obtained was cooled to 55° F., and sufficient ammonium hydroxide was added thereto to convert the cellulose ether phthalate into the form of its phthalyl ammonium salt, thus resulting in dissolution of the silver halide emulsion. The emulsion was then spread upon a glass plate which had been subbed with gelatin, the plate was warmed to set the emulsion to a gel, and it was then transferred to a drying oven where the water was removed from the emulsion layer. The resulting photographic plate was exposed to a photographic negative, following which the plate was developed with a conventional developer, fixed in a neutral hypo fixing bath, treated with dilute aqueous acetic acid for a short time, washed and dried. A positive image of good quality was obtained.

Example 2

.5 part of a cellulose ether phthalate, which had been prepared by phthalylating ethyl cellulose having an ethoxyl content of 45% to a phthalyl content of 16.8%, was suspended in 34 parts of distilled water. The resulting suspension was cooled to 40° F., and, while agitating, ethylenediamine was added drop-wise thereto until solution was effected. There was then added simultaneously to the solution, while vigorously agitating, 17 parts of a potassium bromide solution and 17 parts of a solution of silver nitrate, these solutions having been prepared in the manner described for the preparation of the corresponding solutions in Example 1. This mixture was stirred for 1 minute and there was then added with stirring 100 parts of a 4% solution of the ammonium salt of a cellulose ether phthalate of the same type as employed in the preceding example. The emulsion thus obtained was precipitated in thread-like form into dilute acetic acid, as described in Example 1, and the precipitate was washed with warm water, drained and dissolved in cold water made alkaline with NH_4OH. The emulsion was diluted to give a readily flowable viscosity. The emulsion was then cooled to 50–55° and was coated on a subbed glass plate which had also been cooled. After coating, the glass plate was placed over a hot plate at 125° and subjected to a current of warm air. The coating thereon dried and was exposed to a photographic negative and processed by means of developer, neutral hypo and dilute acid to give a positive image. All the steps of this example where protection of the silver halide was necessary were carried out under darkened conditions.

Example 3

A dispersion of silver halide was prepared as follows, using as the peptizer a phthalic anhydride derivative of gelatin prepared by reacting 100 parts of gelatin with 5 parts of phthalic anhydride by the method described in Example 1 of the Yutzy and Frame U. S. Patent No. 2,525,753. The following solutions were prepared:

Solution A.—25 parts of the gelatin derative, 141 parts of potassium bromide and 1.3 parts of potassium iodide in 1500 parts of water at 60° C.

Solution B.—170 parts of silver nitrate in 1800 parts of water at 62° C.

Solution B was run into agitated solution A over a period of 2 minutes. This step and the remaining steps of preparing and coating the emulsion were carried out under darkened conditions. The dispersion was cooled to 35° C., and there was added thereto 16¼ parts of 2 normal H_2SO_4 lowering the pH to 2.95. The mass was allowed to settle and was decanted. 400 parts of water were added to the coagulum which had been obtained, and the whole was stirred for 5 minutes at 40° C. at a pH of 4.1. The solid particles were again allowed to settle and separated from the liquid by decanting. The solid material was then dispersed at 45° C. with 2.5 normal NaOH for 35 minutes with the pH adjusted to 6.4. The final volume was adjusted to 500 parts by adding water thereto. Also, there was added 0.009 part of allyl thiourea in 18 parts of methyl alcohol, and the mass was heated for 35 minutes at 65° C. It was then cooled to 40° C., dispersed with an equal volume of water and was mixed with a 5% solution of the ammonium salt of a cellulose ether phthalate using 5 parts of the ethyl cellulose phthalate solution to 1 part of the silver halide dispersion, with the temperature of the dispersion 65° F., and that of the cellulose ether phthalate solution 50° F. The cellulose ether phthalate employed was one which had been prepared from an ethyl cellulose having a 45% ethoxyl content to which had been imparted a phthalyl content of 14.3%. The emulsion was thoroughly mixed in a centrifugal mixer and was coated onto a conventional film base. The temperature of the coating roll was 146° F. and of the chill box 135° F., the coating having been carried out at a rate of 40 feet per minute. The emulsion layer was dried in a current of air, the dry bulb temperature thereof being 120° F. and the wet bulb temperature being 75° F. A sample of the coated film was exposed on the I–*b* sensitometer and processed 3 minutes in developer D–19 with the following results:

10/i Speed	0.84
Gamma	1.32
Fog	0.05

Example 4

A silver halide dispersion was prepared as described in Lowe and Gates, Serial No. 768,480, by a peptizing agent prepared by reacting upon casein at an alkaline pH with acetic anhydride and acrylonitrile, whereby acetyl and acrylonitrile groups are introduced into the casein, followed by oxidizing the product with dilute hydrogen peroxide and precipitating the oxidized casein derivative formed by adding acid to the mass to impart an acid pH, such as 4.3, thereto.

Solution A was prepared consisting of 250 parts of a 10% solution of the modified casein in water, 141 parts of potassium bromide, 1.3 parts of potassium iodide and 1500 parts of water, all at a temperature of 60° C. and a pH of 6.0. Solution B was prepared by mixing together 170 parts of silver nitrate and 1800 parts of water, this solution having a temperature of 62° C. Solution B was run into agitated solution A over a period of 10 minutes. The mass was then cooled immediately to 35° C. at a pH of 6.2. There was then added 16½ parts of 2 normal sulfuric acid which imparted a pH of 3, and the precipitate formed was allowed to settle and the liquid was decanted therefrom. There was then added 4000 parts of cold water, the grains were dispersed in the water with stirring for 5 minutes, the pH being 3.5, and then 1 part of 2.5 normal sodium hydroxide was added. The grains were allowed to settle and the liquid was decanted off. 12 parts of 2.5 normal NaOH was then added, which raised the pH from 3.9 to 7.6. The grains were dispersed for 35 minutes at 45° C. The pH was then adjusted to 7.5 with 2 normal sulfuric acid, and the final volume was adjusted to 1000 cc. of the dispersion per mol of silver. The temperature was adjusted to 65° C. and 9 mg. of allyl thiourea per mol of silver halide was stirred into the mass for 30 minutes at that temperature. The material was then cooled to 50° F. and mixed with a 5% solution of the ammonium salt of ethyl cellulose phthalate. This ethyl cellulose phthalate resulted from phthalylating a cellulose ether having an ethoxyl content of 45% to a phthalyl content of 15.4%. The mixing was carried out in a centrifugal mixer in the ratio of 1 part of the silver halide dispersion to 5 parts of the solution of ethyl cellulose ammonium phthalate, the mixed mass being at 50° F. The emulsion mixture was then coated onto conventional film base support as a thin layer, the coating roll and the chill box each having a temperature of 140° F., the coating operation being carried out at the rate of 28 feet per minute. The coated film was then dried with a current of air having a temperature of 100° F. and a wet bulb temperature of 70° F. There was thus obtained a photographic film of the negative type. This film was adapted for exposure and processing by the use of conventional developer and fixing in neutral hypo, followed by treatment with aqueous acid to make sure that the cellulose ether phthalate at this stage is in the acid form.

We claim:

1. A method of preparing photographic products having a silver halide emulsion layer which includes the steps of preparing silver halide in a dispersing agent therefor, forming therefrom a silver halide photographic emulsion in which the silver halide is dispersed in an aqueous solution of a water-soluble salt selected from the ammonium, alkali metal and amine salts of the phthalic, succinic and maleic acid esters of ethyl cellulose having an alkoxyl content of at least 42% which ester has a dicarboxylic acid radical content of at least 5%, coating the emulsion thus prepared onto a support therefor and immediately thereafter applying to the emulsion layer warm air having a wet bulb temperature of at least the setting temperature of the ethyl cellulose ester salt until setting of the emulsion layer is obtained and continuing the application of the warm dry air to the emulsion layer until the layer has dried.

2. A method of preparing photographic products having a silver halide emulsion layer which includes the steps of preparing silver halide in a dispersing agent therefor, forming therefrom a silver halide photographic emulsion comprising grains of silver halide dispersed in an aqueous solution of a water soluble salt selected from the ammonium, alkali metal and amine salts of a phthalate of ethyl cellulose having an alkoxyl content of at least 42%, the ester having a phthalyl content of at least 5%, coating the silver halide emulsion thus prepared onto a support therefor and immediately thereafter applying to the emulsion layer thus formed warm air having a wet bulb temperature of at least the setting temperature of the ethyl cellulose phthalate salt until setting of the emulsion layer is obtained and continuing the application of warm dry air to the emulsion layer until that layer has dried.

3. A method of preparing photographic products having a silver halide emulsion layer which includes the steps of preparing silver halide in an aqueous solution of an ethylene diamine salt of ethyl cellulose phthalate as the dispersing agent, forming therefrom a silver halide photographic emulsion by mixing the silver halide dispersion thus prepared with an aqueous solution of an ammonium salt of a phthalate of ethyl cellulose having an alkoxyl content of at least 42%, the ester having a phthalyl content of at least 5%, as the vehicle for the silver halide, coating the emulsion thus prepared onto a support therefor and immediately thereafter applying to the emulsion layer thus formed warm air having a wet bulb temperature of at least the setting temperature of the ethyl cellulose phthalate salt until setting of the emulsion layer is obtained and continuing the application of warm, dry air to the emulsion layer until that layer has dried.

4. A method of preparing photographic products having a silver halide emulsion layer which includes the steps of preparing silver halide in an aqueous solution of a starch acetate as the dispersing agent, forming therefrom a silver halide photographic emulsion by mixing the silver halide dispersion thus prepared with an aqueous solution of an ammonium salt of a phthalate of ethyl cellulose having an alkoxyl content of at least 42%, the ester having a phthalyl content of at least 5%, as the vehicle for the silver halide, coating the emulsion thus prepared onto a support therefor and immediately thereafter applying to the emulsion layer thus formed warm air having a wet bulb temperature of at least the setting temperature of

the ethyl cellulose phthalate salt until setting of the emulsion layer is obtained and continuing the application of warm, dry air to the emulsion layer until that layer has dried.

5. A method of preparing photographic products having a silver halide emulsion layer which includes the steps of preparing silver halide in an aqueous solution of a phthalic anhydride derivative of gelatin as the dispersing agent, forming therefrom a silver halide photographic emulsion by mixing the silver halide dispersion thus prepared with an aqueous solution of an ammonium salt of a phthalate of ethyl cellulose having an alkoxyl content of at least 42%, the ester having a phthalyl content of at least 5%, as the vehicle for the silver halide, coating the emulsion thus prepared onto a support therefor and immediately thereafter applying to the emulsion layer thus formed warm air having a wet bulb temperature of at least the setting temperature of the ethyl cellulose phthalate salt until setting of the emulsion layer is obtained and continuing the application of warm, dry air to the emulsion layer until that layer has dried.

6. A method of preparing photographic products having a silver halide emulsion layer which includes the steps of preparing silver halide in an aqueous solution of an oxidized casein derivative containing acetyl and acrylonitrile groups as the dispersing agent, forming therefrom a silver halide photographic emulsion by mixing the silver halide dispersion thus prepared with an aqueous solution of an ammonium salt of a phthalate of ethyl cellulose having an alkoxyl content of at least 42% the ester having a phthalyl content of at least 5%, as the vehicle for the silver halide, coating the emulsion thus prepared onto a support therefor and immediately thereafter applying to the emulsion layer thus formed warm air having a wet bulb temperature of at least the setting temperature of the ethyl cellulose phthalate salt until setting of the emulsion layer is obtained and continuing the application of warm, dry air to the emulsion layer until that layer has dried.

7. A photosensitive silver halide emulsion capable of setting in layer form when subjected to elevated temperature which comprises grains of silver halide dispersed in an aqueous solution of a water-soluble salt selected from the ammonium, alkali metal and amine salts of the phthalic, succinic and maleic acid esters of ethyl cellulose having an alkoxyl content of at least 42% which ester has a dicarboxylic acid radical content of at least 5% as the carrier for the silver halide grains.

8. A photosensitive silver halide emulsion capable of setting in layer form when subjected to an elevated temperature which comprises grains of silver halide dispersed in an aqueous solution of a water soluble salt, selected from the ammonium, alkali metal and amine salts, of a phthalate of an ethyl cellulose having an alkoxyl content of at least 42%, the ester having a phthalyl content of at least 5%, as the carrier for the silver halide grains.

9. A photosensitive silver halide emulsion capable in layer form of setting at an elevated temperature which comprises grains of silver halide dispersed in an aqueous solution of an ammonium salt of a phthalate of ethyl cellulose having an alkoxyl content of approximately 45%, the ester having a phthalyl content of approximately 19.8%, as the carrier for the silver halide grains.

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