

April 10, 1934.

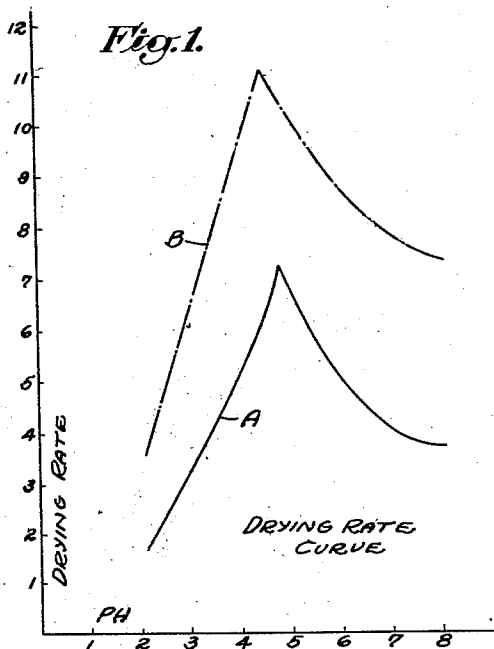
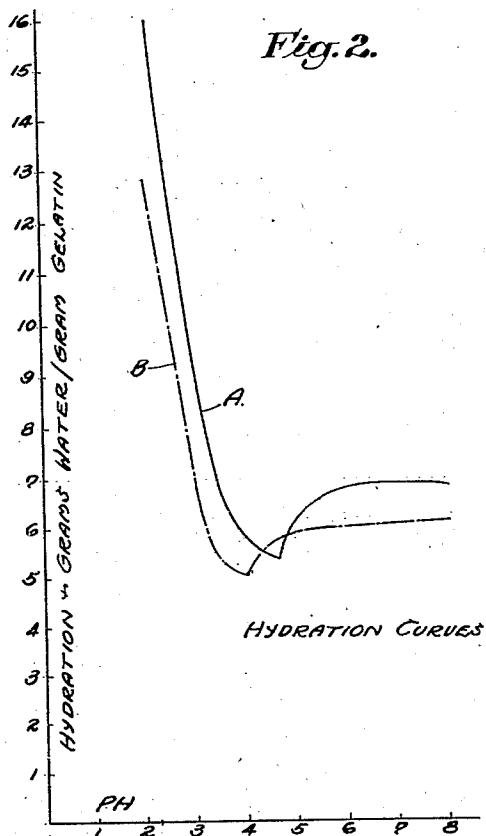
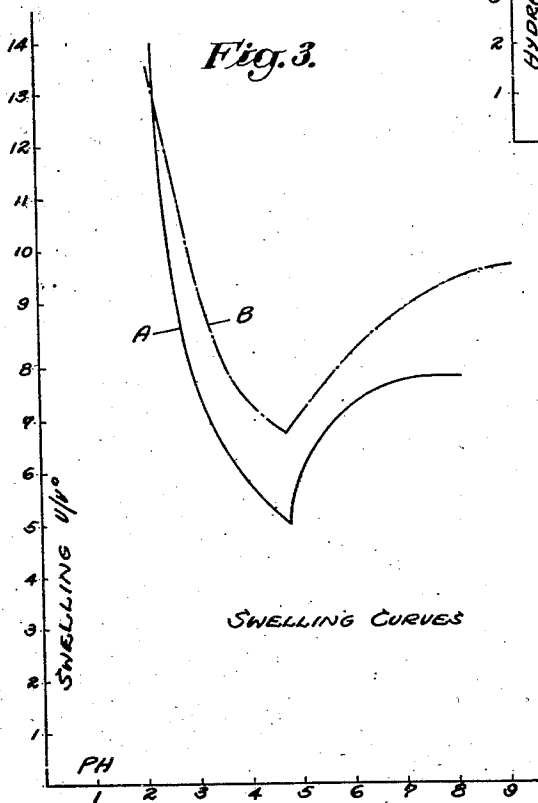
D. K. ALLISON

1,954,512

METHOD OF TREATING OF PHOTOGRAPHIC EMULSIONS

Filed Nov. 28, 1931

2 Sheets-Sheet 1



INVENTOR
Donald K. Allison

April 10, 1934.

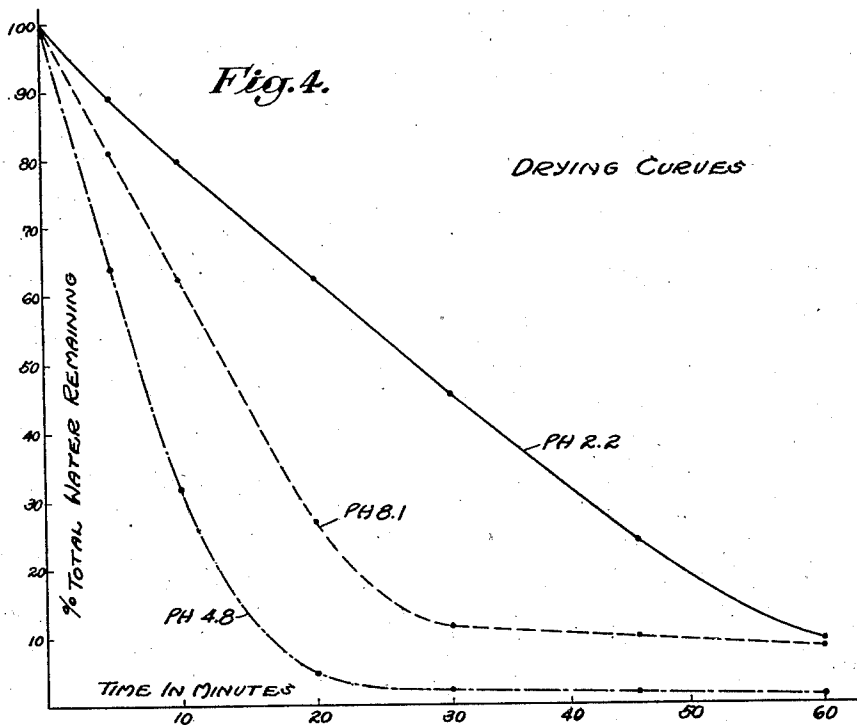
D. K. ALLISON

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METHOD OF TREATING OF PHOTOGRAPHIC EMULSIONS

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2 Sheets-Sheet 2



INVENTOR:
Daniel K. Allison

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METHOD OF TREATING OF PHOTOGRAPHIC EMULSIONS

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of California

Application November 28, 1931, Serial No. 577,749

8 Claims. (Cl. 95—88)

This invention deals with the processing of photographic emulsions and finds its principal application in the art of treating motion picture film where, due to the immense quantity of product handled and the consequent expense necessitated in the construction and maintenance of laboratories for its processing, any substantial saving in time and material is an extremely important factor.

It is, therefore, the general object of my invention to materially decrease the time required in the various steps of processing photographic film of all kinds while at the same time producing a finished film of a quality far superior to that which it is possible to obtain by present day laboratory methods.

More particularly, an object of my invention is to provide a process for producing a film which will dry much more rapidly than film processed by previously known means and which is less susceptible to abrasion during processing, has less residual hydration, a harder final emulsion and is less subject to reticulation.

It is a further object of my invention to provide a process for treating film that will give a more efficient clearing action to the hypo and wash water solutions with the result that less solution is necessary to accomplish the complete treatment of the film and the natural softening and swelling incident to the immersion of the film is materially decreased.

It is a further object to provide a process for coloring film which is more rapid and efficient, and will give a much more transparent image which is at the same time very clear and true in color.

Some of the additional objects and advantages of my invention will appear in the course of the following detailed description of my process.

For the purpose of illustrating a few of the beneficial results obtained by the use of my invention, the results of a portion of my experimental work are depicted in the accompanying curves. To show the applicability of my invention to various types of film, I have chosen at random two of the well-known brands of film on the market, Eastman and Du Pont. In the accompanying graphs the curves representing results obtained from Eastman stock are shown in full lines and identified by the letter "A", while the results obtained from Du Pont stock are shown by a phantom line and identified by the letter "B". In the drawings:

Fig. 1 is a graph showing comparative drying rates for emulsions washed in solutions of various pH values.

Fig. 2 is a graph showing the hydration or relative amounts of water absorbed by gelatin treated with solutions of varying pH values.

Fig. 3 shows the comparative swelling characteristics of emulsions washed at various pH values.

Fig. 4 shows the drying curves (percent of total water remaining in gelatin, plotted against time of drying) for the same film washed at three different pH values.

In the production of a finished film the accepted procedure, broadly speaking, is to develop the exposed film, fix it, and give it a final wash. If it is to be colored, this step is usually separate and distinct. My invention is an improvement on this general procedure in treating the film and is applicable equally well to the many variations in methods of treating film which are prevalent in the industry. As will be disclosed, I am able by a modification of present practices to obtain many beneficial effects without a radical and expensive change from present day procedure.

In producing a negative by the practice of my invention, I first expose a sensitized negative film in any of the well known cameras on the market today and secure thereby a latent image of the subject photographed. Similarly in making a positive or final film I print from a finished negative onto a sensitized positive film by any of the well known printing methods. Taking the exposed film, either positive or negative as the case may be, I then develop the latent image by the use of a developer such as hydroquinone, elon or metol in combination with suitable alkalies such as sodium tetraborate, sodium carbonate and the like, the choice of developer depending on the type of film used and the particular characteristics desired in the finished film. Following development a brief water-wash is usually given the film. This wash water may be maintained at the isoelectric point of the gelatin of the emulsion as hereinafter described. From the wash, the film is then passed into a fixing solution commonly known as "hypo", the one most universally used being a solution of sodium thiosulphate, sodium sulphite and a hardening agent such as potassium chromium sulphate ("chrome-alum"), or formaldehyde.

To this standard fixing solution I add sufficient acid, preferably acetic or some similar weak acid, until the pH i. e.

$$\left(\log_{10} \frac{1}{\text{Hydrogen ion concentration}} \right)$$

of the solution is brought to and maintained at the isoelectric point of the particular gelatin used. As a result of extensive experiments on the subject, I have found that a distinct advantage is gained by holding the pH at approximately this critical point, and that while a slight acidification is beneficial, if the solution is acidified beyond the isoelectric point of the gelatin, the beneficial effects are negated so that an

excess of acid gives the same result as no acid at all.

Experiments show that by thus maintaining the pH of the fixing solution at the isoelectric point of the gelatin being treated, I get a much more efficient clearing action which means less hypo solution required, a much shorter time required in the treatment and less residual silver halide in the resultant emulsion.

If a hardener is used in the hypo, or as a separate step in the process, similar advantages are obtained by holding the pH at the isoelectric point of the gelatin permitting less hardener to be used and a wider variation in the temperature of the solution with a harder resultant emulsion which, because of its increased hardness, has better wearing properties and is less susceptible to the abrasion incident to projection and handling.

When the film has remained in the fixing solution a sufficient length of time to thoroughly clear the residual halide from the emulsion, it is given a complete water wash to remove the remaining hypo from the film. Inasmuch as the pH of ordinary water averages around 8.0 and is seldom below 7.0, and as the isoelectric pH of standard gelatins is around 4.8, it is necessary to lower the pH of the wash water to this point. This I do by the addition of any acid having a dissociation constant sufficiently high to lower the pH of the wash solution to the isoelectric point of the gelatin. It is to be understood, however, that if by chance the wash solution should have a pH lower than the isoelectric point of the particular gelatin, I would add a suitable alkali to bring the pH up to the isoelectric point; in other words, my invention contemplates not merely acidifying solutions, but rather the regulation and control of the pH at the isoelectric point. By maintaining the pH at this critical point, I find that I get much more efficient washing in that the salts are eliminated from the emulsion much more rapidly with less water being required for the wash.

The most important and valuable result of regulating and controlling the pH at the isoelectric point of the gelatin is, however, that in the drying of the film it is found that the time required for a satisfactory dehydration is greatly reduced as shown by the curves in Figs. 1 and 4. In fact, exhaustive tests have shown that the drying time after washing at the critical point is approximately fifty per cent less than the drying time after washing with ordinary water which usually has a pH of approximately 8.0, and that there is correspondingly less residual hydration in the emulsion. If the rate of drying is plotted against the pH of the treating solution as illustrated in Fig. 1, it is found that the portions of the curve immediately adjacent the isoelectric value show almost a straight line relationship between rate of drying and pH, the slope of the curve changing sign at the isoelectric value, giving a maximum drying rate at this point on the curve, the slope between 4.0 and 4.8 being approximately equal in value to the slope between 4.8 and 5.9 with a reversed sign.

Inasmuch as the isoelectric point of gelatin varies with the characteristics of the gelatin composition, it is, of course, necessary for extremely accurate work to predetermine this point by proper tests of film of the same type and make as the film to be processed. This predetermination can be done by any of the methods well known to colloidal chemists and forms no part

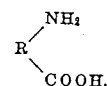
of this invention. It will be found that most of the commercial gelatin on the market is sufficiently similar so that for mass production satisfactory results will be obtained by a treating solution that is regulated to the average isoelectric point of such standard gelatins.

For example, I have found that the optimum pH value for the treating of Eastman duplitized positive stock varies from 4.6 to 4.9 although varying degrees of improvement are noted between as wide limits as 3.5 to 7.0. On the other hand, the optimum pH for Du Pont stock varies from about 4.4 to 4.7 with a corresponding relation between wider limits. For the large laboratory then, the pH of treating solution could well be regulated at approximately 4.6, thus being within the optimum range for both emulsions.

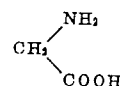
If it is also desired to color the film by any of the well known processes such as selective chemical toning or die-toning, I maintain the pH of the toning, mordanting and dyeing solutions at the isoelectric point of the gelatin by the addition of the proper amounts of acid. In the case of chemical toning less chemicals are needed, and in the case of dye-toning the same advantage obtains with a much more transparent image produced in either case. Furthermore, in the dye-tone method there is no danger of an overall stain, as it is substantially impossible to stain isoelectric gelatin with either acid or basic dyes.

There are certain beneficial effects which result from the maintenance of the pH of any treating solution at the isoelectric point of the gelatin being treated which should be noted, namely that as illustrated in Figs. 2 and 3 the emulsion is not softened or swollen as much as it is by the use of a solution of different pH, and there is much less danger of reticulation.

One theory for the phenomenal results obtained by the practice of my invention is based on the premise (now generally conceded by colloidal chemists to be true) that gelatin is to be principally composed of several amphoteric amino acids, such as glycine, leucine, histidine, arginine, etc. all of the type



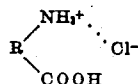
of which glycine



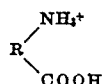
is the simplest, and a typical example. In the case of gels, consider these amino acids to be so oriented or polymerized as to form a felted lattice structure, having a myriad of interstices or cells which are permeable to water and most ions by osmosis, but the nature of the gelatin lattice being such that the molecules of the amino acids are firmly held in place. These amphoteric amino acids react both as acids and bases and the point at which their acidic and basic properties are equal and the molecule exhibits electroneutrality is defined as their isoelectric point. Most gelatins have an isoelectric point near pH 4.7. It is important to note that not all of the amino acids composing gelatin will have an isoelectric point at pH 4.7, but the gelatin "molecule" as a unit reacts as though it were a single molecule of acid having a definite isoelectric point. Since this point is only an average value, it cannot be sharply defined, as variations in the relative proportions of the amino acids may cause a shift or

spreading of the isoelectric pH value. Further, the behavior of the various individual acids will prevent an absolutely isoelectric property, since at least some of the amino acids will possess active properties at any pH value representing an average point for all of the constituent acids. For practical purposes, however, we may assume an isoelectric point at pH 4.7.

In solutions of pH less than 4.7, the gelatin will react as a base, and salts of gelatin are formed such as gelatin chloride

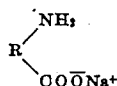


in the case where the treating solution contains hydrochloric acid. These salts are largely ionized, but the impermeability of the gelatin lattice to gelatin prevents diffusion of the gelatin cation



and electrostatic forces of the gelatin chloride molecule prevent diffusion of the chloride anion, with the result that the concentration within the gelatin lattice becomes higher than that outside, and osmotic forces arise which are compensated only by diffusion of water into the lattice, with corresponding hydration, swelling, etc.

In solutions with a pH value greater than 4.7, gelatin reacts as an acid and, for example, if the solution predominates in sodium hydroxide, salts of the type of sodium gelatinate

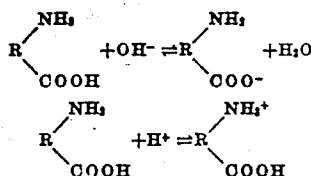


are formed. Again the lattice structure prevents diffusion of the gelatin anion



and electrostatic forces prevent diffusion of the sodium cation, so that the osmotic forces cause diffusion of water into the lattice, and again we observe hydration, swelling and attendant phenomena.

In solutions of pH 4.7, i. e. the isoelectric value, the gelatin as a whole becomes neutral, a minimum of gelatin salts are formed, osmotic forces are minimal with resultant minimal swelling and hydration. It should be noted, however, that at pH 4.7 some salts are formed, since it is very unlikely that all of the amphoteric amino acids present in gelatin would have isoelectric properties at pH 4.7. I have stated, therefore, that the aforementioned properties of gelatin become minimal at pH 4.7. It is generally conceded that the acidic and basic properties of gelatin follow the mass action law, so that the concentration of gelatin salt and the gelatinate formed in the reactions:



may be both expressed as functions of pH, the

function depending on the mass action expression for the reaction. Since it is the concentration of gelatin salt or gelatinate, as the case may be, which determines the osmotic forces, we have a quantitative explanation of the behavior of gelatin at various pH values.

The drying time depends, of course, on the amount of water to be removed and the rate of removal. As shown above, the amount of water absorbed by the gelatin is a function of the pH and is a minimum at the isoelectric point of the gelatin. Similarly it will be noted that the drying rate will obviously be a function of the ease with which we can remove the water from the interstices of the gelatin lattice. Therefore, if the gelatin has been washed with water having some pH value other than 4.7, the high osmotic forces within the gelatin lattice tending to hold water in the lattice will greatly retard drying. On the other hand, if the emulsion has been washed with water of pH at or near 4.7, the osmotic forces tending to hold water in the gelatin lattice become minimal, and the drying rate, therefore, becomes maximal.

Similarly, in washing gelatin emulsions, the efficacy of the wash will depend largely on the rate of circulation of wash water through the gelatin. Therefore, at a wash water pH other than 4.7, the distended gelatin lattice, because of its greater thickness, increased viscosity and high osmotic forces tending to hold the wash liquid in the gelatin lattice instead of allowing it to carry away the undesirable impurities, presents a serious disadvantage to efficient washing. At wash water pH values at or near 4.7, these above mentioned disadvantages are greatly reduced, and washing efficiency thereby increased.

The efficiency of other processes, such as chemical toning of the silver image, removal of the unreduced silver halide of the photographic emulsion by sodium thiosulphate solution, (commonly known as hypo), etc., will be in a large measure hampered by the same factors discussed in relation to washing, namely, increased thickness and viscosity of emulsion and osmotic forces in the gelatin lattice tending to prevent circulation through the gelatin, when the process solutions have a pH value other than 4.7. When the pH of the process solution is maintained at or near 4.7, these disadvantages largely disappear, and the process thereby becomes more efficient.

Although I have discussed my invention only in its application to photographic film, it is to be understood that it is equally applicable to the treatment of all types of photographic emulsion wherein the sensitive element is composed of gelatin impregnated with a sensitizing salt, it being further understood that the foregoing theory for the results obtained by my invention is for the purpose of explanation only and forms no part of my invention nor limits it in any manner.

I claim as my invention:

1. In a process for treating photographic emulsions the step which comprises maintaining the pH of the treating solution at approximately the isoelectric point of the gelatin being treated.
2. In a process for producing a visible photographic image from a latent photographic image, the step which comprises maintaining the pH of the fixing solution at approximately the isoelectric point of the gelatin bearing the image.
3. The method of cleaning a developed and

fixed photographic image which comprises washing said image in a solution having a pH approximating the isoelectric point of the gelatin bearing said image.

- 5 4. In a process for coloring photographic images, the step which consists in maintaining the pH of one of the coloring solutions at approximately the isoelectric point of the gelatin bearing the image being colored.
- 10 5. A method of treating an exposed photographic film which includes: subjecting said film to a treating solution having a pH approximately equal in value to the isoelectric point of the gelatin on said film.
- 15 6. A method of treating an exposed photographic film which includes: washing said film in a solution while maintaining the pH of said solution at approximately the isoelectric point of the gelatin on said film.

7. A method of treating an exposed photographic film which includes: treating said film with a developing solution to bring out the latent image thereon; subjecting said film to the action of a solution containing sodium thiosulphate; and washing said film in a solution having a pH approximately equal in value to the isoelectric point of the gelatin carrying said image.

8. A method of treating an exposed photographic film which includes: treating said film with a developing solution to bring out the latent image thereon; subjecting said film to the action of a solution containing sodium thiosulphate; washing said film in a solution having a pH approximately equal in value to the isoelectric point of the gelatin carrying said image and removing substantially all of the water from said film and the gelatin thereof.

DONALD K. ALLISON.

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