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2,367,549

PHOTOGRAPHIC SILVER HALIDE EMULSION

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FIG. 1.

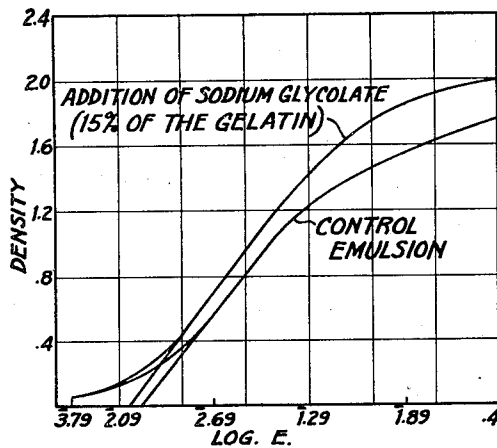


FIG. 2.

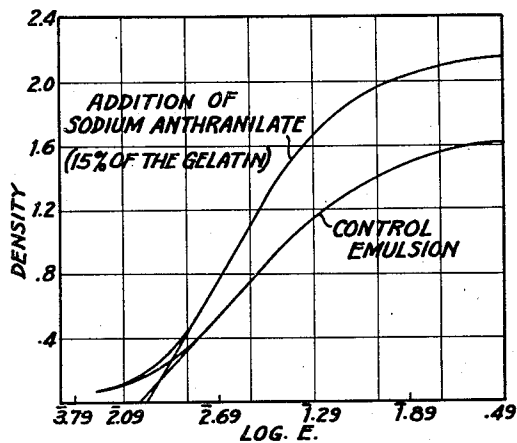
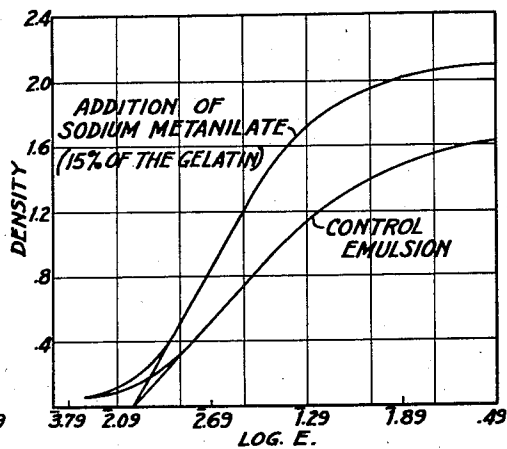


FIG. 3.

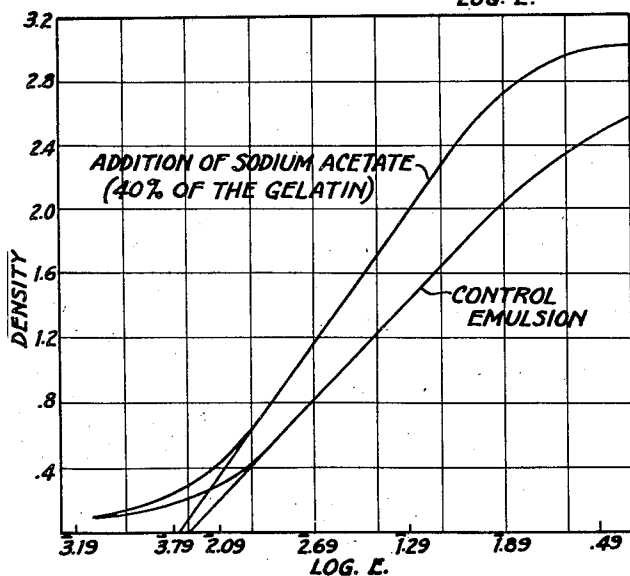


FIG. 4.

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PHOTOGRAPHIC SILVER HALIDE
EMULSIONS

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14 Claims. (Cl. 95—7)

This invention relates to sensitive photographic emulsions, and more particularly to a method for improving the sensitometric characteristics of such emulsions.

Salts in light sensitive silver halide emulsion layers have long been a subject of discussion in the art. It has long been a practice to wash photographic emulsions to free them of salts formed during emulsion making, for instance, in order to increase the sensitivity of the emulsions. On the other hand, salts of acids such as acetic, adipic, etc., have been used as buffers in emulsions with beneficial results.

I have found that if salts of the organic acids of my invention are used in sufficient quantities in emulsions they improve the sensitometric characteristics of the emulsions, such as gamma and speed. Thus the addition of soluble salts of organic acids to photographic emulsions causes an increase in the development rate. This is particularly true when these emulsions are developed in relatively high potential developers. Therefore, for a given time of development an increase in gamma, and often an increase in effective speed as well, is obtained with emulsions containing such addenda. On the other hand, for development to equal gammas, an emulsion coating containing an addendum as above will require a shorter time of development than a similar emulsion coated without any addendums. Furthermore, it has been found that these salts cause an increase in gamma infinity and the maximum density that is obtained on development of the exposed emulsion.

It is, therefore, the object of the present invention to provide organic acid salts which may be used in silver halide emulsion layers to improve sensitometric characteristics.

Salts which may be used are the ammonium, amine, or alkali metal salts of acids such as acetic, tartaric, citric, particularly hydroxy monobasic acids, such as lactic, glycolic, mandelic, gluconic and glyceric; benzene sulfonic acid and its substitution products, such as the amino benzene sulfonic acids—metanilic, sulfanilic, and orthanilic; benzoic acid and its substitution products, such as anthranilic and salicylic acids. Other substitution products of benzene carboxylic and sulfonic acids, such as o, m or p-bromobenzoic, o, m or p-chlorobenzoic and 2,5-dichlorobenzene-sulfonic are likewise effective.

The method I use for incorporating the salts of my invention into emulsions, consists of dissolving the acid furnishing the required anion in alkaline solution or dissolving the required pre-

formed salt in water, and adding this solution with or without the addition of an organic solvent such as alcohol, to the emulsion at some stage in its manufacture. A convenient method is to add the salt solution to a melted gelatin-silver-halide emulsion just prior to coating. As cations for the salts I may use bases furnishing ammonium, amine or alkali metal ions.

I have found that the quantity of salt used in an emulsion is a critical factor in the respect that if too little is used, its sensitometric characteristics such as gamma and speed will not be appreciably affected. The following data show the effect of using varying quantities of sodium acetate, based on the amount of gelatin, in a sensitized emulsion. Development was for the same time in a high potential developer.

20	Percent sodium acetate	10/i speed	Gamma	Fog
	Control.....	1,150	0.92	.07
	30.....	955	1.39	.05
	15.....	1,060	1.19	.05
	7.5.....	1,010	1.11	.05

25 Thus, if the salt is present in an amount such as is customarily used in buffer solutions, that is, less than about 5 per cent of the weight of the gelatin, little or no change in sensitometric characteristics will be observed when such an emulsion is compared with a control emulsion containing no salt. The quantity I use is from about 5 per cent-25 per cent, preferably about 15 per cent, of the weight of the carrier material, if gelatin is used. Similar quantities may be used for emulsions having carriers other than gelatin.

30 The effect of the salts on emulsion characteristics is better understood by reference to the accompanying drawing, wherein Figs. 1, 2, 3, and 4 show by graphical representation the effect of typical salts on sensitometric characteristics such as gamma and speed.

In the drawing, Fig. 1 shows by means of H and D curves, the sensitometric characteristics of a non-color sensitized bromiodide control emulsion before addition of sodium glycolate, and after the salt has been added (15 per cent salt on the weight of gelatin). Both emulsions were given the same time of development in a high potential developer. It is observed that if the straight-line portion of the curves are extended to the abscissa, a comparison of the gamma and speed may be made. It is apparent that in this case the salt has been instrumental in causing an increase in both speed and gamma.

Fig. 2 shows the effect of adding 15 per cent of the weight of gelatin of sodium metanilate to a high-speed emulsion. It may be seen that the gamma and speed of the treated emulsion, as shown by the curve to the left, is considerably higher than that of the control emulsion.

Fig. 3 shows the H and D curves of two emulsions, to one of which has been added 15 per cent sodium anthranilate. The effect of the addition of the salt to the emulsion is to produce a considerable increase in gamma and an increase in speed which is not as great in the toe region as it is along the straight-line portion of the curve, as calculated by well-known methods which recognize that at the same inertia speeds different gammas give at the same density different speeds, such as astronomical speeds.

Fig. 4 illustrates in a similar manner the effect of adding sodium acetate to an emulsion. The particular control emulsion, the H and D curve of which is shown at the right in the figure, was an optically sensitized emulsion having a 10/i speed of 1070, gamma 1.03, and fog .08. When sodium acetate was added in the amount of 40 per cent of the weight of the gelatin to the control emulsion, the speed was 1200, gamma 1.39 and fog .09. Development was carried out in a high potential developer for the same time in each case.

Example

To show the relative effect of certain salts on emulsion characteristics the following experiments are given.

To an ordinary unsensitized gelatin-silver halide emulsion the following salts were added in the amount of 15% of the weight of gelatin in the emulsion. The results tabulated are for development of each emulsion for the same time in Kodak D-19 developer.

	10/i speed	Gamma	Fog
Control.....	525	1.25	.06
Potassium acetate.....	570	1.50	.06
Potassium glycolate.....	640	1.32	.05
Sodium citrate.....	510	1.49	.08
Sodium tartrate.....	550	1.43	.07
Sodium salicylate.....	545	1.47	.05
Sodium lactate.....	590	1.73	.06
Ammonium benzoate.....	575	1.65	.06

It is to be noted that the "10/i method" of obtaining emulsion speeds (as described in Shepherd U. S. Patent 2,184,023, granted December 19, 1939) is subject to certain limitations and is not applicable in all cases to give a clear picture of the effect of salts giving curves such as shown in Fig. 2 and Fig. 3. Other methods which recognize that at the same inertia speeds different gammas give at the same density different speeds, such as astronomical speeds, are more suitable. Computations made by these methods show that in the regions of higher density there are speed differences between two given emulsions, whereas, the 10/i method might show little or no difference in speeds.

I have found that the effect of the salts in my invention on emulsion characteristics is not limited to a specific type of emulsion. Emulsions whether non-sensitized, optically or chemically sensitized, are favorably affected. The salts differ somewhat in their ability to improve sensitometric characteristics. For instance, the same control emulsion was used for the experiments the results of which are shown in Fig. 2 and Fig. 3, and it is apparent that the improvement in gam-

ma and speed is different in each case. The same is true of isomeric salts such as sodium metanilate and sodium sulfanilate. Similarly, different substitution products of the salts of the acids of my invention give different types and degrees of improvement of sensitometric characteristics of emulsions. Simple experiments illustrate the effect of such salts on emulsion characteristics.

It is to be understood that the disclosure herein is by way of example and that I consider as included in my invention all modifications and equivalents falling within the scope of the appended claims.

What I claim is:

1. The method of improving the sensitometric characteristics of a gelatino-silver halide emulsion which comprises adding to said emulsion from 5% to 25% of the weight of the gelatin in the emulsion of a salt having a cation selected from the group consisting of ammonium, amino and alkali metal, and an anion selected from the group of acids consisting of benzoic acid and its amino, hydroxyl and halogen substitution products, and benzene sulfonic acids and the halogen and amino substitution products thereof.

2. The method of increasing the gamma of a gelatino-silver halide emulsion which comprises adding to said emulsion 5 to 25 per cent of the weight of the gelatin in the emulsion of a salt having a cation selected from the group consisting of ammonium, amino and alkali metal, and an anion selected from the group of acids consisting of benzoic acid and its amino, hydroxyl and halogen substitution products, and benzene sulfonic acids and the halogen and amino substitution products thereof.

3. The method of improving the sensitometric characteristics of a gelatino-silver halide emulsion which comprises adding to said emulsion from 5% to 25% of the weight of the gelatin in the emulsion of a water-soluble salt of an acid selected from the group consisting of ammonium, amino and alkali-metal salts of benzene sulfonic acid and the halogen and amino substitution products thereof.

4. The method of increasing the gamma of a gelatino-silver halide emulsion which comprises adding to said emulsion from 5% to 25% of the weight of the gelatin in the emulsion of water-soluble salt of an acid selected from the group consisting of ammonium, amino and alkali-metal salts of benzene sulfonic acid and the halogen and amino substitution products thereof.

5. The method of increasing the gamma of a gelatino-silver halide emulsion which comprises adding to said emulsion from 5% to 25% of the weight of the gelatin in the emulsion of an alkali metal salt of metanilic acid.

6. The method of increasing the speed of a gelatino-silver halide emulsion which comprises adding to said emulsion 5 to 25 per cent of the weight of the gelatin in the emulsion of a salt having a cation selected from the group consisting of ammonium, amino and alkali metal, and an anion selected from the group of acids consisting of benzoic acid and its amino, hydroxyl and halogen substitution products, and benzene sulfonic acids and the halogen and amino substitution products thereof.

7. The method of improving the sensitometric characteristics of a gelatino-silver halide emulsion which comprises adding to said emulsion from 5% to 25% of the weight of the gelatin in the emulsion of a water-soluble salt selected from the group consisting of ammonium, amino, and

alkali metal salts of an acid selected from the group consisting of benzoic acid and its amino, hydroxyl and halogen substitution products.

8. The method of increasing the speed of a gelatino-silver halide emulsion which comprises adding to said emulsion from 5% to 25% of the weight of the gelatin in the emulsion of ammonium benzoate.

9. The method of increasing the gamma and speed of a gelatino-silver halide emulsion which comprises adding to said emulsion 5 to 25 per cent weight of gelatin in the emulsion of a salt having a cation selected from the group consisting of ammonium, amino and alkali metal, and an anion selected from the group of acids consisting of benzoic acid and its amino, hydroxyl and halogen substitution products, and benzene sulfonic acids and the halogen and amino substitution products thereof.

10. The method of increasing the gamma and speed of a gelatino-silver halide emulsion which comprises adding to said emulsion from 5% to 25% of the weight of the gelatin in the emulsion of a water-soluble salt of an acid selected from the group of acids consisting of benzene sulfonic acid and halogen and amino substituted ammonium, amino and alkali-metal salts of benzene sulfonic acids.

11. The method of increasing the gamma and

speed of a gelatino-silver halide emulsion which comprises adding to said emulsion from 5% to 25% of the weight of the gelatin in the emulsion of an alkali metal salt of sulfanilic acid.

12. A silver halide emulsion comprising as an agent for improving the sensitometric characteristics thereof, 5 to 25 per cent of the weight of the gelatin in the emulsion of a salt having a cation selected from the group consisting of ammonium, amino and alkali metal, and an anion selected from the group of acids consisting of benzoic acid and its amino, hydroxyl and halogen substitution products, and benzene sulfonic acids and the halogen and amino substitution products thereof.

13. A gelatino-silver halide emulsion comprising as an agent for increasing the gamma thereof, from 5% to 25% of the weight of the gelatin in the emulsion of a water-soluble salt of an acid selected from the group consisting of ammonium, amino and alkali-metal salts of amino benzene sulfonic acids.

14. A gelatino-silver halide emulsion comprising as an agent for increasing the speed thereof, from 5% to 25% of the weight of the gelatin in the emulsion of a water soluble salt selected from the group consisting of ammonium, amino, and alkali metal salts of benzoic acid.

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