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PROCESS OF PHOTOGRAPHIC DEVELOPMENT

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This invention relates to photographic developers and a method of photographic development, and is, in part, a continuation of my application Serial No. 196,366, filed March 17, 1938, entitled "Photographic developer."

It has heretofore been customary to develop sound record negative film in ordinary positive developer or in a modification thereof, thereby producing a negative having the same relative characteristics as a picture positive or having these characteristics very slightly modified. This procedure has been highly undesirable, particularly with variable area sound records, where an extreme density of the exposed area is desired, together with complete freedom from fog in the unexposed areas and strict proportionality of density in the area of graded exposure produced due to the finite width of the exposure aperture adjacent to the exposed area.

In addition to the foregoing, a developer for this purpose must be satisfactory for use in the tanks of continuous developing machines; it must have a relatively long life, i. e., must not age too rapidly; and it must maintain its developing action substantially constant during its period of usefulness.

Heretofore, no developer has been available having the foregoing characteristics. My improved developers have all of the foregoing characteristics and, in addition thereto, is extremely inexpensive, decreasing the developer cost, per foot of film, to only a small fraction of the previous cost.

In the preparation of my improved developer, I make use of the peculiar characteristic of certain metallic salts which permits them to act as a "buffer" and to maintain the effective alkalinity of the developer bath substantially constant during its life.

One object of my invention is to provide an improved method of photographic development.

Another object of my invention is to provide an improved method of maintaining the alkalinity effectively constant during development.

Another object of my invention is to provide an improved method of removing deleterious materials from the developer during development.

Another object of my invention is to provide an improved method of removing exhausted developing material from the developer during development.

Another object of my invention is to provide an improved method of maintaining the effective strength of the developer constant by maintaining its volume constant.

Another object of my invention is to provide an improved method of maintaining equilibrium between the rate of development of photographic material and the rate of replenisment of developer physically removed and developer chemically exhausted.

Another object of my invention is to provide an improved method of maintaining a developer at constant effective developing power by replenishment of the developer with a developing solution of the same composition and strength as the original developer.

Another object of my invention is to provide an improved method of preventing reticulation and clumping of silver grains by hardening the emulsion material in the developer.

Another object of my invention is to provide an improved method of hardening emulsion material.

Another object of my invention is to harden emulsion material in an alkaline developer.

Other and incidental objects of my invention will be apparent to those skilled in the art from a reading of the following specification.

The objects are accomplished according to my invention by adding a metallic compound, such, for example, as potassium alum, to the developing solution, and using an alkali in sufficient quantity to dissolve or redissolve the precipitate which tends to be, or is, first formed.

My invention, in its broad aspect, is applicable to developers containing practically any of the usual developing agents which function in alkaline solution, and also is adapted to the use of any of the usual alkalies, although some developing agents and some alkalies are preferable to others.

For example, a very rapid developer is necessarily quite alkaline. In order to produce a proper buffering balance of the alum in this highly alkaline solution, it is accordingly necessary to use a large quantity of alum. Under this circumstance, if a sodium carbonate, for example, is used as alkali, the total solids in the solution become extremely great, in order to maintain the same constant alkalinity in the manner described in detail hereinafter, and I therefore prefer to use sodium hydrate.

Materials used

Although I have above referred to the use of alum in developer, I find that a number of other materials may be used. The aluminum, for example, may be introduced in the readily available form of potassium aluminum sulphate, known generally as alum, or any other convenient water soluble aluminum salt may be used, such, for example, as aluminum sulphate, aluminum chloride, or aluminum bromide. Although aluminum is the metal which I have found to be usually most desirable for my purpose, I find that appropriate salts of either zinc, tin, chromium or lead may also be used. These various metallic salts produce different degrees of effect with different developing agents, and, although I have found aluminum quite satisfactory with all developing agents which I have tried, some of the other metals produce too high or too low a reducing power to be generally satisfactory, although they are all operative with all of the available developing agents. Lead salts, in general, appear to produce a somewhat unstable balance in the developer and increase the speed of development for any given developing agent quite considerably over that obtained with the other salts mentioned or with none of them. The chromium compounds are not as satisfactory as aluminum compounds due to the instability of the chromium compounds produced in the developer which tend to precipitate out with them. Tin and zinc vary the developing power with certain developers to a greater extent and with others to a lesser extent than the aluminum.

The aluminum compounds produce sufficient tanning action on the gelatine, or prevent the softening action of the alkali to such an extent, that I have found it practical to use the developer including aluminum up to a temperature of well over 105° F., at which temperature the developer becomes very uncomfortable to handle. As compared to this, previous developers containing an equivalent quantity of developing agent and alkali completely remove the emulsion from the backing at a temperature as low as 80°.

In the preparation of my improved developers, I used somewhat less than the usual proportion of sodium sulphite for the reasons that, first, a large quantity of sulphite is not necessary, and, second, the reduction in quantity of sulphite decreases the solution of silver salts and redeposition thereof which produces diffusion of the image in developers high in sulphite.

In order to preclude any material effect upon the developer due to the production of alkali bromide in the solution during development, I prefer to initially provide in the solution such a quantity of bromide that further addition of bromide during the reactions causes no material change in the effect thereof. This effect of bromide is described in "Theory of Development," by A. H. Nietz, published by the Eastman Kodak Company, Rochester, New York, and D. Van Nostrand Company, New York, 1922, pages 150 to 152. Optimum concentration for bromide to produce this constancy of effect is .08 mol. per liter.

The developing agent may be, so far as I have been able to ascertain, any usual or customary photographic developing agent. For example, the following developing agents have been satisfactory used with each of the aforementioned metals:

Hydroquinone (para-hydroxyphenol)
Glycine (para-hydroxyphenylglycine)
Metol (mono-methyl-para-amino-phenol)
Paraphenylenediamine (para-diamino-benzene)
Bromo-hydroquinone (2-brom-4-hydroxy-phenol)
Tolu-hydroquinone (2-methyl-4-hydroxy-phenol)
Catechol (1-2-hydroxy-benzene)
Dichlor-hydroquinone (2-3-chlor-4-hydroxy-phenol)
Chlor-hydroquinone (2-chlor-4-hydroxy-phenol)
Duratol (para-benzyl-amino-phenol)
Pyro (1-2-3-hydroxy-benzene)
Amidol (2-4-diamino-phenol)
2-amino-5-hydroxy-toluene
Para-amino-phenol
Phenyl-hydrazine
Hydroxylamine-hydrochloride

It seems evident that reducing agents of the following characteristics are also satisfactory: Any benzene derivative whose reduction potential lies within the range ordinarily desired for a photographic developer. The number of possible substitutions in benzene derivatives is practically unlimited. Nuclear substitutions need be made such as in chlor-hydroquinone. Side chain substitutions need be made as in para-dimethyl-amino-phenol where methyl groups are substituted in the amino group. Side chain substitutions may be extended to the addition of further benzene rings. This is encountered in Duratol. Another derivative related to Duratol would be para-dibenzyl-amino-phenol, where a double substitution is made in the amino group.

According to "Theory of Development" (supra) the effect of substitutions in the benzene derivatives used as developers have as their effect only the alteration of the energy of the organic reducing agent. Certain substitutions might make the developing energy so great that the compound would not be practical. Certain nitro substitutions might do this. In general, substitutions involving the following groups are permissible without seriously altering the developer energy:

Hydroxide	Ethyl
Halide	Carboxyl
Amino	Benzene
Methyl	

These groups may be substituted singly or in combination.

Preparation of the developer

Certain of the developing agents require different treatment to get them into solution in the most suitable manner. For example, metol must be dissolved in water before sulphite is added. Hydroquinone must be protected by the presence of sulphite before sodium hydroxide is added, that is, for the best results. Duratol will not dissolve without the presence of sodium hydroxide. These examples merely indicate that there is a variation in the properties of the various developing agents. In general, it is possible to dissolve the developing agent simultaneously with sodium hydroxide. Sodium sulphite is added to the solution, as is potassium bromide or a suitable halide salt, to act as a restrainer. The order of admixture of the various components of the developer is immaterial. If, however, the relative quantity of the buffer metallic salt and the alkali are unknown, then the admixture must be made in such a fashion that a proper balance can be observed, that is, the precipitate which first tends to be or is formed by the metallic salt is redissolved by adding an appropriate quantity of alkali. The balance between this precipitate and the alkali is produced when the metallic precipitate is just redissolved.

The alum and alkali may, if desired, be dissolved separately and then mixed, or the alum may be dissolved first and the alkali added afterward, or vice versa, according to which is most convenient. However, if sodium hydrate is used, the quantity thereof must be approximately the same as that of the alum, whereas if the carbonate is used, the quantity thereof must be of the order of four times the quantity of the alum, depending upon the degree of hydration of the carbonate.

The developing agent may be mixed in a quantity amounting to approximately $\frac{1}{7}$ to $\frac{1}{16}$ gram molecular weight per liter. The amount of developer used is determined by the desired developer speed or reaction velocity. Sodium sulphite is added as a preservative in a quantity amounting to approximately $\frac{1}{4}$ mol. per liter or more. The concentration of sulphite is not critical, and should be not less than 1 molecule of sulphite for each molecule of developer.

Sodium hydroxide is, as pointed out above, used as an energizer, and the quantity of this is determined by the characteristics desired in the developer. The usable concentrations range from below 10 grams per liter to above 300 grams per liter.

The sodium hydroxide is balanced with an appropriate amount of alum determined as follows: Powdered alum is slowly added to the solution containing hydroxide. As addition of the alum is continued, the rate of solution slowly decreases until the point is reached where further addition of alum produces no further solution, leaving undissolved alum crystals. Conversely, the alum may be dissolved first and the sodium hydroxide added later. In this case, the initial addition of sodium hydroxide produces a precipitate of aluminum hydroxide which is redissolved on further addition of sodium hydroxide, and when this precipitated aluminum hydroxide is just redissolved the solution is in proper equilibrium. The appropriate amount of potassium bromide may be added to the solution at any time during preparation thereof. The addition of other substances to the developing solution for other or incidental purposes is within the scope of my invention provided only that the aforesaid balance between the aluminum content and alkali content is maintained.

Although I have described the preparation of a developer including alum, the same method is used in the preparation of a developer containing any of the other metals referred to.

The following formula illustrates a satisfactory composition which I have used:

Na_2SO_3	grams	50
p-hydroxyphenyl Glycine (Glycin)	do	20
NaOH	do	25
$KAl(SO_4)_2.12H_2O$	do	30
Water to make	ccs	1000

For maximum contrast with this developer, 10 grams of potassium bromide should also be added.

Another example of the application of my invention in a developer which has been found useful is the following:

Hydroquinone (para-dihydroxybenzene)	grams	15
Na_2SO_3	do	17
$KAl(SO_4)_2.12H_2O$	do	38
NaOH	do	30
KBr	do	10
Water to make	ccs	1000

The first of the above developer formulas, although rather concentrated and therefore rather high in first cost, will, nevertheless, develop film of the type described at an extremely low cost. This is due to the fact that whereas the ordinary types of metol-hydroquinone developers heretofore used are effective for approximately 20 feet of film per liter of developer, with appropriate replenishment of the developer in the meantime, my improved developer will serve to develop approximately 250 feet of film with the same loss of strength, corresponding to a decrease of approximately .2 in the density of the finished film. As compared to the prior developers used on sound film which, with the customary exposure, would develop the film to a density of the order of 1.9, my improved developer will produce a density of approximately 2.1 on the sound negative, and the sound prints can be exposed and developed to the correspondingly high density of 2.35 (as against 1.4) with a minimum of zero shift in the sound track, "zero shift" being the term applied to the shifting of the zero point of high frequencies in accordance with their amplitude, as described in the article entitled "Modulated High Frequency Recording as a Means of Determining Conditions for Optimal Processing," by J. O. Baker and D. H. Robinson, Journal of the Society of Motion Picture Engineers, volume 30, No. 1, January 1938. Further, the high frequency loss, for example at 9000 cycles, with my developer is no greater at these high densities than at the lower densities attained with the prior art developers.

The film footage per liter above referred to is such that no replenishment of the developer is required in ordinary film developing machines. The film runs through the machine at a speed of the order of 180 feet per minute, and a compressed air jet is used to blow adhering developer from the film back into the tank. In spite of this jet, a certain amount of developer adheres to the film, and this residual adhering developer is a quantity of the order of magnitude of the developer used in developing the film. By adjusting the pressure on this compressed air jet or blow-back the rate of carry-over of the developer may, if desired, be made substantially identical with the rate of exhaustion of developer. If fresh developer is then added to the tank at such rate as to retain the fluid level constant, the developing solution will reach a state of equilibrium which will be thereafter maintained.

The second developer formula given above has the advantage over the first formula in that it is somewhat less expensive and requires a development time, in a developing machine, of the order of four minutes, as against nine to eleven minutes for the first formula.

Operation of the developer

The reaction of the organic reducing agent with the exposed silver bromide in the film produces a shift in ion concentration through a long chain of reactions. When the developer is oxidized by silver bromide, Br^- ions are released. Aluminate ions exist from the reaction

$$2KAl(SO_4)_2+6NaOH \rightleftarrows K_2SO_4+3Na_2SO_4+2Al(OH)_3 \rightleftarrows$$

$$Al(OH)_3+NaOH \rightleftarrows NaAlO_2+2H_2O$$

It is understood that each and every compound indicated in the above reaction will form certain ions in solution. For example, the alum in solution would produce potassium ions, aluminum ions and sulphate ions. The sodium aluminate indicated would, in solution, produce sodium ions and aluminate ions. It is evident from the above reaction, which is really a mass reaction balance consisting of three reactions, that there will be present in the solution a large number of different ions.

From chemical functions known to the art, it will be apparent that the above reaction will reach a state of equilibrium depending on the molecular proportions of the several elements, tending in the direction indicated by the heavy arrows. Any change in alkalinity of the solution will shift the equilibrium point one direction or the other, depending on whether the alkalinity is increased or decreased. As indicated in the above reaction, if the alkalinity is decreased, the equilibrium point will be shifted to the left.

The only thing that keeps the $Al(OH)_3$ in solution is an excess of NaOH. The presence of Br^- ions would shift the balance of the above reaction slightly to the left. $Al(OH)_3$ is now better able to combine with the gelatine of the film to harden it, as in any tanning action. Thus the film (gelatine) in the near neighborhood of the developed image undergoes a pronounced hardening which is evidenced by a distinct lack of swelling of the gelatine.

As the supply of free alkali is converted into salts in course of development, free alkali is liberated by the aluminum-alkali compound or complex, thereby maintaining the alkalinity effectively constant. At the same time the aluminum hydroxide or other metallic hydroxide which is freed forms a gelatinous precipitate which entraps exhausted developing material and other foreign material which may be in the developer and carries all of this suspended material out of the solution in the manner well known in water purification by the use of aluminum salts. The developing solution is thereby maintained at all times free from the exhausted material which tends to form scum, spots, stains or fog on the film in the developers of the prior art.

This coagulation of aluminum and deleterious material may be either permitted to settle to the bottom of the developing container and removed therefrom at convenient intervals or the developer may be passed into a separate settling tank or container from which the sediment may be removed from time to time. Since the addition of fresh developer of the original composition does not tend to redissolve the aluminum as the addition of a stronger solution, such as generally used for enrichment of developer, would do, this precipitate does not tend to become finely divided or redissolved, and it is therefore readily removed from the zone of operations in the manner before described. This greatly decreases the cost of operation of developing machines as compared to the present procedure wherein the developer is filtered under high pressure and through complicated filtering mechanisms in order to remove exhausted developing material. Of course, with my improved developer and method of development, a filter may be used if desired, but the filter required, due to the large size and gelatinous nature of the material to be removed, is very much simpler than that required for removing the fine suspended particles from the usual commercial types of developer.

A further advantage of my improved developer is that if the aforesaid gelatinous precipitate is not removed, but is kept in suspension in the solution by mechanical agitation, either through the passage of the film through a relatively small quantity of solution or otherwise, this gelatinous precipitate does not shown the tendency to adhere to the film, which is common to the materials in suspension in a partly exhausted developer of the usual type. In other words, a considerable portion of such material is removed from a developing machine by the blow-back and any residual material which may adhere to the film is easily removed in the rinse water, leaving no spots or stains whatever on the film.

It will be apparent from the foregoing that, in addition to a new developer, I have provided a novel method of removing foreign materials from the developer during the operation, a novel method of maintaining the developer at effectively constant alkalinity, and a novel method of maintaining the developer at constant effective developing properties.

I claim as my invention:

1. The method of maintaining the alkalinity of a photographic developer effectively constant comprising substantially balancing the alkali content of the developer with a salt of a metal of the group consisting of aluminum, chromium, tin, lead and zinc at such a point that the alkali in the developer is just sufficient to keep the said metal from precipitating in the form of hydroxide, and releasing alkali by precipitation of a salt of the metal of such group as alkali is required.

2. The method of maintaining the alkalinity of a photographic developer effectively constant comprising substantially balancing the alkali content of the developer with alum at such a point that the alkali in the developer is just sufficient to keep the aluminum from precipitating in the form of hydroxide, and releasing alkali by precipitation of aluminum hydroxide as alkali is required.

3. The method of maintaining both the alkalinity and the effective strength of a photographic developer effectively constant and of hardening emulsion material in an alkaline developer, preventing reticulation or clumping of silver grains and removing deleterious materials from the developer, comprising substantially balancing the alkali content of the developer with a salt of a metal of the group consisting of aluminum, chromium, tin, lead and zinc at such a point that the alkali in the developer is just sufficient to keep the said metal from precipitating in the form of hydroxide and releasing alkali by precipitation of a salt of the metal of such group as alkali is required, the said precipitate being gelatinous in nature and carrying down the deleterious materials from the developer, removing an amount of developer corresponding to the exhaustion thereof by adhesion to the developed material, and simultaneously adding an equivalent amount of a fresh developer of the original strength.

4. The method of maintaining the alkalinity of a photographic developer effectively constant comprising adding an excess of alkali to the developer, substantially balancing the alkali content of the developer with alum at such a point that the effective alkalinity is just sufficient to keep the resulting aluminum salt in solution, and releasing alkali by precipitation of aluminum hydroxide.

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