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PROCESSING PHOTOGRAPHIC PAPER AND FILM

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This invention relates to methods of shortening the time required for processing exposed sensitized photographic materials such as paper, film, foil, glass and the like.

Many attempts have been made in the past to expedite the processing of photographic materials. One frequently attempted method has involved increasing the temperatures of the developing and fixing media to hasten the reduction of silver salts to metallic silver and the dissolution of unreduced silver salts; however, due to mechanical problems involved in applying hot solutions to photographic materials, such efforts have usually failed when tried on a commercial basis. Other attempts to hasten the processing have involved the forceful application of the processing media to the emulsion-coated surfaces of the photographic materials as by sprays, but there have almost always been concomitant difficulties stemming out of the problems involved in applying a uniform spray without the benefit of elaborate equipment; also, under such circumstances, there is ordinarily a tendency to oxidation of the chemicals by atmospheric oxygen. Other attempted methods of shortening the processing time have involved the incorporation in the emulsion of one or more of the chemicals commonly used in processing; e. g., hydroquinone, but the addition to the emulsion of the usual processing chemicals tends as a rule to impair the photographic image and its keeping qualities. Still other methods have sought to effect desensitization of undeveloped silver salts remaining after development; such methods have usually fallen short of success because of the failure of the desensitizer to do an adequate job of desensitizing and/or to prevent solarization of the undeveloped silver salts.

Even where these or like expedients have been attempted, the reduction in processing time, although sometimes significant, has in general not been enough to bring the processing time down to a matter of seconds rather than minutes.

The principal object of the present invention is to provide methods of shortening the times required for processing photographic materials to an extent such that processing can be accomplished, if desired, in a matter of a few seconds. It is also an object of the invention to accomplish these ends by the use of not more than two processing media. It is a further object of the invention to reduce the processing time in the manner and to the extent indicated without making use of elaborate equipment to induce super-atmospheric temperatures, pressures and other abnormal conditions. It is still a further object of the invention to make use of media that are stable under ordinary conditions. Still a further object of the invention involves the production in situ in the finished product, in addition to metallic silver, of light-insensitive silver salts and development by-products that are transparent, translucent or innocuous for other reasons.

Other objects of the invention will become apparent as the description of the invention proceeds.

In the tests made in connection with the present invention it has been found that these objects may be successfully accomplished by (*a*) providing an emulsion-coated water-resistant photographic material in which, along with the light-sensitive silver salt or salts, the usual gelatine-base emulsion incorporates one or more added accelerators of development; (*b*) exposing to form a latent image; (*c*) converting the latent image to a visible image by subjecting the exposed material for a few seconds at ordinary room temperatures to the action of an alkaline-

reacting water solution of a developer normally considered to be a weak developer; (*d*) converting to innocuous form the undeveloped silver salt or salts remaining in the photographic material by subjecting it for a few seconds' time at ordinary room temperatures to the action of an acid-reacting water solution of a selected water-soluble stabilizer; and (*e*) drying the stabilizing material in any convenient manner, as by permitting adherent water to evaporate into the atmosphere.

These steps may be elaborated, if desired, as by introducing a washing step and/or drying at elevated temperatures in conventional drying equipment.

Preliminary, the photographic material is coated, if necessary, to render it non-absorptive to water, which is desirable in order to expedite drying subsequent to processing. If the photographic material has a base of film, foil, glass or the like, no separate steps are necessary, but if it consists of water-absorbent paper or cloth, it is preferably coated with lacquer at least on the side to which no emulsion will be applied, but preferably on both sides, so as to minimize the possibility of absorption of water. This may be done by treating the uncoated material in known fashion. Assuming the use of a photographic paper which has been coated on both sides with a suitable lacquer, such as a nitro-cellulose, cellulose acetate, ethyl cellulose or polyvinylbutyral lacquer, the next step is to apply to one side of the paper a gelatine-base emulsion similar to any one of the gelatine-base emulsions commonly used for photographic purposes but including one or more development accelerators along with the gelatine, light-sensitive silver salt or salts, and other usual ingredients.

Assuming that it is desired to prepare a photographic paper of the contact type, one may mix together 25 grams of sodium chloride, 8 grams of citric acid, 150 grams of gelatine and 1700 grams of water, stirring thoroughly while heating to about 60° C. to melt the gelatine. There is then added a solution of 50 grams of silver nitrate in 300 grams of water, the added solution being introduced at or about 45° C. The resulting mixture should be ripened for 45 minutes at about 60° C. Thereafter 50 grams of gelatine dissolved in 600 grams of water are added at about 60° C., after which the whole is cooled and brought up to a total volume of 3200 cc. by the addition of more water. According to ordinary commercial practice, this or a similar mixture is then applied to the paper and dried to form the emulsion layer.

A photographic paper of the projection type involves the preparation of a first solution comprising 66 grams of potassium bromide, 5.75 grams of potassium iodide, 30 grams of gelatine and 1250 grams of water, to which is added a second solution of 97.5 grams of silver nitrate in sufficient water to make 200 cc. Before the solutions are combined by pouring the second into the first, the second is modified by adding ammonium hydroxide (specific gravity 0.880) until the precipitate just redissolves at room temperature and, after having done so, raising the temperature of the solution to about 65° C. Thereupon the second solution is added to the first solution at about 65° C. and the resulting mixture is allowed to ripen at that temperature for 30 minutes. Thereafter 100 grams of gelatine are added and the whole is allowed to ripen for an additional 15 minutes at about 65° C. The mixture is cooled to room temperature after ripening, is allowed to set, and is washed to a pH of about 7.0.

The product is then shredded and 25 cc. of a 20 percent solution of potassium bromide in water is added along with enough additional water to bring the total volume to 2000 cc.

Emulsions produced as described above are typical of conventional silver halide emulsions in the sense that they do not include the accelerator or accelerators of development that are included in accordance with the teachings of the present invention. Such an accelerator may take the form of a water-soluble inorganic salt such as nickelous chloride, cadmium chloride, uranium chloride, gold chloride, rhodium chloride, platinum chloride, osmium chloride or the like. In lieu of the chloride, the salt may in suitable cases take the form of the sulphate, nitrate or acetate, although where the latter salts are insoluble they should not be used. The introduction of

one or more of these salts or their equivalents is believed to modify the potential sensitivity of the silver salt or salts to light. At any rate, one or more of these salts may, if desired, be introduced into emulsions of the types above described by adding 8 to 12 and preferably about 10 grams of the salt per kilogram of emulsion. The salt is added in the form of a water solution at a temperature of about 45° C. (contact paper) or about 65° C. (projection paper) immediately after the silver nitrate is added, the quantity of water used as a solvent for the salt being held to a minimum.

In lieu of or together with such water-soluble inorganic accelerator of development may be used an organic accelerator of development of the nature of a dyestuff having a capacity for modifying the potential light-sensitivity of the silver salt or salts. The materials that are useful for this purpose are those described at pages 1042 to 1046 of C. E. K. Mees' "The Theory of the Photographic Process," published in 1942, by MacMillan & Company at New York, N. Y., and, in particular, the desensitizers identified therein as the anils, phenosafranines, pinakryptol greens and pinakryptol yellows. Whether they desensitize in a particular case is immaterial for present purposes, although desensitization is often a desirable incidental feature. It will be noted that although these materials include certain nearly colorless compounds such as those sold under the name of pinakryptol yellow, they are all of the nature of dyestuffs.

These organic accelerators of development may be added at or slightly above room temperatures; e. g., 35° C., to the emulsion before its application to the paper. Preferably they are added in the form of a methanol solution, 1:1000, in the amount of 300 cc. of solution per gallon of emulsion. If desired, however, the emulsion may be made up in the usual way, applied to the paper and allowed to harden, after which the organic accelerator of development may be applied as a superficial or topical application or bath in the form of the methanol solution at a temperature of about 35° C. Other methods of incorporation include the addition of the methanol solution to the photographic emulsion in the course of the mixing operation, the temperature of the methanol solution being matched to that of the emulsion if practicable.

From what has already been said, it will be apparent that inorganic and organic accelerators of development may be used either alone or together. Preferred practice involves the use of both, in which case the inorganic accelerator of development is included in the emulsion at the time the emulsion itself is made and the organic accelerator of development is introduced as an additive at any convenient time before or after coating. Thus a photographic material of the kind employed in the process of the invention includes one or the other or both of the two kinds of development accelerators. The precise nature of their action is not understood, but it may be that they are or can be considered to be catalysts.

The photographic material having been prepared as described, the next step is to expose it in the usual way to form a latent image, there being no departure from conventional practice at this stage.

Thereafter the process of the invention contemplates conversion of the latent image to a visible image by subjecting the exposed photographic material for a matter of a few seconds' time at ordinary room temperatures to the action of a suitably compounded developing medium. The latter takes the form of a strongly alkaline-reacting water solution of an especially selected developer. Along with the developer itself, the developing medium contains sodium hydroxide, sodium sulphite and water.

The developing medium must have two unusual properties: (1) it must reduce the exposed silver halide to metallic silver in an extremely short time and (2) when reducing the silver halide, it must create products which are colorless, nearly colorless, or gaseous. To accomplish the first requirement, the developing medium contains a large enough quantity of alkali to raise the pH to approximately 12 and contains no restrainer, which is usually potassium bromide. The second requirement can be met most readily by the use of a developing agent which oxidizes to water and gas. Since the developer will remain in the emulsion as both exhausted developer and unused developer, it is desirable that both forms of the developer be colorless or gaseous or non-active photographically in the finished print.

Hydroxylamine hydrochloride, hydrazine hydrochloride and phenylhydrazine hydrochloride will meet the latter requirements provided that the final pH is below 6. Other like materials may be used in addition to or instead of them. The named developers are usually considered to be weak developers in that normally they require from five to ten minutes' time to convert the latent image to a satisfactory visible image, although in the process of the present invention this is done in a matter of a very few seconds, usually not more than two to three seconds. As therein used, hydroxylamine hydrochloride, hydrazine hydrochloride and phenylhydrazine hydrochloride bring about rapid change of the latent image to a visible image by chemical reduction of silver salt to metallic silver.

Formulations for the developing medium are:

	Grams
(1) Hydroxylamine hydrochloride (Practical)	20
Sodium hydroxide (USP)	22
Anhydrous sodium sulphite (USP)	50
Water to make 1000 cc.	
(2) Hydrazine hydrochloride (Practical)	20
Sodium hydroxide (USP)	22
Anhydrous sodium sulphite (USP)	50
Water to make 1000 cc.	
(3) Phenylhydrazine hydrochloride (Practical)	20
Sodium hydroxide (USP)	22
Anhydrous sodium sulphite (USP)	50
Water to make 1000 cc.	

Thereafter it is necessary to impart the quality of permanence to the image by converting to innocuous form any undeveloped silver salts remaining in the emulsion layer, which is best done by subjecting the photographic material for a few seconds' time at ordinary room temperatures to the action of a stabilizing medium. Preferably the latter consists of an acid-reacting aqueous solution of a water-soluble salt of an inorganic halogen or halogenoid acid selected from a group consisting of iodic acid, fluoric acid and thiocyanic acid. With the salt is preferably used an organic acid such as acetic acid, tartaric acid, citric acid or some other organic acid of comparable hydrogen-ion concentration the action of which is to terminate development. The action of the water-soluble iodide, fluoride or thiocyanate or like salt is to convert the undeveloped silver salt into a photographically insensitive compound in which the silver is transparent, translucent or almost white, which is sufficiently stable, and which does not require fixing or washing out unless time permits and it is desired to add a separate fixing step, a separate washing step or both.

Examples of formulations for the stabilizer are as follows:

(1) Potassium iodide (USP)	grams	100
Acetic acid (glacial)	cc	100
Water to make 1000 cc.		
(2) Potassium thiocyanate (USP)	grams	100
Acetic acid (glacial)	cc	100
Water to make 1000 cc.		
(3) Potassium fluoride (USP)	grams	100
Citric acid (USP)	do	75
Water to make 1000 cc.		

Where, in keeping with the teachings of the invention, a stabilizer of the kind above described is employed, the image that has been produced in the development step will be relatively stable, will not be materially degraded by the chemicals remaining in the photographic material after completion of the processing operations, and will not darken through reduction, solarization or other like process of deterioration. Whereas with most other types of developers and stabilizers, the necessary inertness cannot be communicated to the undeveloped silver salts, the developing and stabilizing media contemplated by the present invention as typified by the examples and formulations given above do not in normal usage result in appreciable degradation of the image even though they are permitted to remain in the emulsion in a dry state for great lengths of time.

As will be apparent from what has already been said, departures from the preferred practices hereinabove described are within the purview of the invention. In its fundamentals, however, the invention includes the introduction of an inorganic accelerator of development and/or an organic accelerator of development of the nature of a dyestuff in or to the emulsion; immersion of the photo-

graphic material for a few seconds' time in a developing medium which serves to convert the latent image to a visible image without deleterious by-effects; conversion of the undeveloped silver salts to innocuous form by introducing the developed photographic material into a stabilizing solution of one of the kinds described whereby the processing chemicals themselves remain innocuous; and, at minimum, drying under any convenient conditions. Drying may, if desired, be preceded by a fixing step, a washing step, or both, although neither is necessary and the effect of using them is of course to increase the processing time. Where, as is contemplated, the steps of fixing and washing are omitted, development and stabilization can both be accomplished in a matter of not more than five seconds' total immersion in the developing and stabilizing media.

It is intended that the patent shall cover, by summarization in the appended claims, whatever features of patentable novelty reside in the invention.

What is claimed is:

1. A method of shortening the processing time of photographic material comprising the steps of (*a*) providing an emulsion-coated photographic material in which the emulsion coating incorporates a light-sensitive silver halide and an organic accelerator of development having a capacity for affecting the light- and development-characteristics of the silver halide, said organic accelerator of development being a desensitizing dye-stuff selected from a group consisting of the anils, phenosafranines, pinakryptol greens and pinakryptol yellows; (*b*) exposing the material to form a latent image; (*c*) converting the latent image to a visible image by subjecting the exposed material for a few seconds at room temperatures to the action of an alkaline-reacting water solution of a developer selected from a group consisting of hydroxylamine, hydrazine and phenylhydrazine, said alkaline-reacting solution having a pH approaching 12; (*d*) converting to inert form the undeveloped silver halide remaining in the material by subjecting the developed material for a few seconds at room temperatures to the action of a stabilizer taking the form of an acid-reacting aqueous solution of an alkali metal salt of an acid selected from a group consisting of iodic acid, fluoric acid and thiocyanic acid; and (*e*) drying the stabilized material.

2. A method of shortening the processing time of photographic material comprising the steps of (*a*) providing an emulsion-coated photographic material in which the emulsion coating incorporates a light-sensitive silver halide and an inorganic accelerator of development taking the form of a water-soluble salt of a metail selected from a group consisting of nickel, cadmium, uranium, gold, rhodium, platinum and osmium; (*b*) exposing the material to form a latent image; (*c*) converting the latent image to a visible image by subjecting the exposed material for a few seconds at room temperatures to the action of an alkaline-reacting water solution of a developer selected from a group consisting of hydroxylamine, hydrazine, and phenylhydrazine, said alkaline-reacting solution having a pH approaching 12; (*d*) converting to inert form the undeveloped silver halide remaining in the material by subjecting the developed material for a few seconds at room temperatures to the action of a stabilizer taking the form of an acid-reacting aqueous solution of an alkali metal salt of an acid selected from a group consisting of iodic acid, fluoric acid and thiocyanic acid; and (*e*) drying the stabilized material.

3. A method of shortening the processing time of photographic material comprising the steps of (*a*) providing an emulsion-coated photographic material in which the emulsion coating incorporates a light-sensitive silver halide and an inorganic accelerator of development taking the form of a water-soluble salt of a metal selected from a group consisting of nickel, cadmium, uranium, gold, rhodium, platinum and osmium and an organic accelerator of development having a capacity for affecting the light- and development-characteristics of the silver halide, said organic accelerator of development being a desensitizing dye-stuff selected from a group consisting of the aniles, phenosafranines, pinakryptol greens and pinakryptol yellows; (*b*) exposing the material to form a latent image; (*c*) converting the latent image to a visible image by subjecting the exposed material for a few seconds at room temperatures to the action of an alkaline-reacting water solution of a developer selected from a group consisting of hydroxylamine, hydrazine, and phenylhydrazine, said alkaline-reacting solution having a pH approaching 12; (*d*) converting to an inert form the undeveloped silver halide remaining in the material by subjecting the developed material for a few seconds at room temperatures to the action of a stabilizer taking the form of an acid-reacting aqueous solution of a water-soluble salt of an acid selected from a group consisting of iodic acid, fluoric acid and thiocyanic acid; and (*e*) drying the stabilized material.

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