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ELIMINATION OF PRESERVATIVE SULFITE FROM PHOTOGRAPHIC DEVELOPERS PRIOR TO USE IN COLOR DEVELOPMENT

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This invention relates to photographic development processes and is particularly concerned with the photographic process of colour development in which a dye image and a silver image are simultaneously produced when a photographic latent image or silver salt image is treated in a bath containing a coupling developer and usually also a colour coupler, and to other processes in which it is also an advantage to have no sulphite present in the developer bath, for example in tanning developers, and provides a means whereby the preservative sodium sulphite generally employed in photographic developing solutions to protect the reagents from autoxidation and possibly premature coupling in the solution to dyestuff may be removed just prior to or simultaneously with the development process. It is well known that sodium sulphite competes with the colour coupler in such baths for the developer oxidation products and the amount of dyestuff produced during the development of the image is therefore smaller when sulphite is present than when it is absent. Accordingly it is one object of the invention to employ the sulphite for its preservative action as long as possible but to remove it from the sphere of reaction before a substantial amount of colour development or tanning development has begun, thus securing the greatest possible production of dyestuff, or tanning, or both.

Accordingly the present invention provides a process of photographic development using an aqueous developing solution containing a sulphite as a preservative wherein the sulphite is removed from the solution before any substantantial development or colour formation has begun.

In my application Serial Number 580,327 the method of determining the amount of dyestuff produced in the image as compared with the amount of silver was described and illustrated examples were provided based on measurements of optical density, that of the dye being measured through a filter of approximately complementary colour to the colour of the dye. The ratio of dye density to silver density in the same area of the image was termed the colour factor and in the interests of efficiency it is desirable to secure as high a colour factor for the process as possible.

Means to enable the dye density and the silver density to be separately measured are known. Preferably the tests are made with a series of step-wise exposures provided by a sensitometer and after developing the film strip, if that is the

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material in use, is divided along its length, one half being treated in Farmer's solution to remove the silver and leave only the dye, and the other half being treated for as long as necessary, perhaps for two hours, in a 2% solution of sodium hydrosulphite in order to remove the dye without affecting the silver. The last step may alternatively be omitted and the combined dye and silver densities read. Subtraction of the dye densities on the first half of the strip from the values of the combined densities on the second half will then provide the silver densities.

Sulphites in a developing bath can be oxidized by additions of oxidizing agents such as bromine, sodium hypochlorite, potassium ferricyanide, ferric chloride, ceric sulphate, and alkaline hydrogen peroxide, and their conversion to sulphates destroys their competitive effect against the colour coupler.

The effect of sulphite on the colour factor was illustrated in the aforesaid application Serial Number 580,327 where a factor of 2.75 was obtained with sulphite present and of 5.0 in its absence. In the same application it was stated that sulphite, if present, could be eliminated by the addition of oxidizing agents although in the process of that application an excess of such oxidizer is used over that theoretically required to oxidize the sulphite in order to obtain an oxidation product of the aromatic diamine used as developing agent, such oxidation products if intermediate between the fully reduced diamine form and the fully oxidized holoquinone leading again to an improved colour factor. In the aforesaid application also the method of removing the sulphite by precipitation with barium chloride, or by the use of such aldehydes as form addition compounds with the sulphite was mentioned. All of these methods for sulphite removal furnish the means whereby in accordance with the present invention the sulphite in a colour coupling developer bath or in a tanning developer bath is eliminated from reaction at the actual time of development. Such elimination may be effected whether or not it is intended to use an oxidized or unoxidized aromatic diamine as developing agent, or if another type of coupling developer altogether is preferred, for example an aminophenol. Furthermore it is equally useful to remove the sulphite from those developers which lead to dyestuff and silver images without the further addition of colour couplers, these developers being known as primary colour developers and are reviewed in the Photographic Journal, vol. 85B, pp. 19–20. It

is well known also that pyro developers which are essentially of this type will only give a stain image in the absence or near-absence of sulphite. This same type of developing substance, namely that which of itself leads to an insoluble oxidation product deposited image-wise within the photographic layer during the process of development without the presence of a separate coupling body is frequently also a tanning developer. That is to say, it will render the gelatine of the photographic layer insoluble in hot water at the places of development to silver so that if the resulting image is subjected to a washing treatment with hot water the undeveloped portions will be etched away leaving an image in relief which may be used as a matrix for dye transfer processes. Such a procedure is well known and is the basis of commercial processes of colour photography. The tanning developer baths suitable for these processes normally contain little or no sulphite as this substance acts as an acceptor for the developer oxidation products and if it were preesnt in quantity no tanning would be obtained. In the absence of sulphite the developing solutions employed are subject to extreme oxidation by air and become unusable in a relatively short period. If, however, some sulphite is included in such baths they are much more stable and by means of the present invention the sulphite may be removed at a suitable moment before development starts or has proceeded very far. Examples of developing agents in this class are pyrogallol, pyrocatechol, and hydroquinone, all used in fairly concentrated alkaline solutions.

The removal of the sulphite may be secured by soaking the photographic material being processed in a solution of a barium salt at some convenient stage. For example, a bath of about 30 seconds' duration in a 10% solution of barium chloride or other soluble barium compound or compound of an alkaline earth metal may precede the developer bath containing the sulphite it is desired to remove, which bath should be of about the same duration but it may be desirable to allow the imbibed developer solution to remain in the film for a longer period, say three or five minutes, before washing out. Obviously no specific times can be given as so much depends upon concentrations of reactants, the sensitive material undergoing development, and so forth, and they must be determined by trial and error in each case. Instead of applying the sulphite precipitant to the film it may be added in calculated quantity to the developer bath itself just before use so that the solution has the advantage of sulphite protection until the last moment.

Two-bath methods for development are sometimes used commercially and perhaps one of the most useful aspects of the invention is its application to these. For instance, in a coupling development process the developing agent with sulphite may be used in the first bath and a solution containing the colour coupler and the alkali as well as the sulphite-precipitant or acceptor in the second bath. For primary colour developers or tanning developers the second bath would of course contain only alkali and sulphite-precipitant or acceptor. Especially useful in two-bath development is a second bath containing barium hydroxide. This is a strong alkali and will also precipitate sulphites. Calcium hydroxide and strontium hydroxide may also be serviceable but their solubility is not so high.

However, they might be used in conjunction with a more soluble alkali and the solution could be maintained in a saturated condition with respect to them by having them in excess in a solid condition in the developing bath. For this purpose they might be suspended in the solution in bags made of filter cloth and be present in the form of compressed blocks. When the compounds of these alkaline earth metals are employed it is desirable when other alkalies are present they are not in the form of carbonate or of any salt which would precipitate the alkaline earth metal more readily than does the sulphite which it is necessary to remove. Suitable alkalies are sodium hydroxide, potassium hydroxide, ammonium hydroxide, tribasic alkali phosphates, borates, and organic amines. If desired the solutions may be buffered to a definite pH value, this applying to the alkaline earth hydroxides as alkali as well as to the more usual photographic developer components.

As indicated in my application Serial No. 580,327 a two-bath development process is also possible using an oxidizing agent for the removal of sulphite. If such a reagent is applied to the photographic material in advance of the developer it may be necessary to choose it with care to prevent considerable destruction of the latent image. In redevelopment processes or reversal development this effect is not so serious. When the oxidizer is applied after the application of the developing agent it is obvious that it should be used before the colour coupler is applied in order to prevent a general deposition of dyestuff; or if the coupler is already incorporated in the film the application of the alkali last of all will ensure that no dyestuff is formed in the bath, especially if the first bath was on the acid side of neutral.

Sulphites are also removed from solution by certain aldehydes and ketones. A well-known type of photographic developer uses this reaction for the formation of alkali to activate development, the bath containing acetone and sodium sulphite. No other alkali is needed.

In all of these cases, and as pointed out in the application previously mentioned, the bath used to remove the sulphite may be quite separate from the other processing baths so that the usual two-bath procedures would then become three-bath processes and so on, and, as before, the sulphite may be dealt with by some form of applicator carrying the necessary reagents instead of in an actual bath.

The operation of the processes of this invention entails the precipitation of the sulphite in one of the processing baths or sometimes in the film itself but in most cases this causes no trouble. Any slight deposit on the photographic sensitive material may usually be removed by means of a bath of dilute acid such as one of half per cent acetic acid having no detrimental effect upon the images being developed. When the image has subsequently to be hot-water etched the presence of a slight deposit of, say, barium sulphite is immaterial.

The following examples illustrate how the process of the invention may be carried into effect and the advantages thereof:

Example 1

A silver salt image obtained by bleaching a fixed silver image to silver bromide by the usual means was developed in each of the two solutions prepared as shown under (i) and (ii) and

the colour factors obtained were respectively 4.2 and 2.4.

(i) 2-amino-5-diethylamino toluene

HCl	gm.	0.13
Sodium sulphite anhydrous	gm.	0.20
Potassium bromide 10%	ml.	0.30
Water to	mls.	80

Before use add 4 mls. of 10% barium chloride and stir. Then add 10 mls. of 10% ammonium hydroxide (obtained by diluting 0.880 ammonia ten times) and 8 mls. of the colour coupler solution made up in the form of a 1% solution in alcohol of 2:4-dichlor-1-naphthol.

(ii) As (i) but omit the barium chloride.

Example 2

The first solution was the same as Example 1 (i) but before use 0.13 gm. sodium peroxide was stirred in then the solution was neutralized with about 0.2 ml. of concentrated hydrochloric acid so that no differences should arise due to the extra alkalinity. The solution must then be made alkaline to a normal extent and 8 mls. of 30% sodium carbonate (cryst.) are added and colour coupler as before. An equivalent amount of hydrogen peroxide is more convenient than the sodium body. In this example latent photographic images were developed in the bath.

Example 3

This illustrates the two-bath method. A silver salt image was bleached to silver bromide then re-developed in colour by six minutes' treatment in each of the two baths (i) and (ii) used in succession.

(i) 2-amino-5-diethylamino toluene

HCl	gm.	1.3
Sodium sulphite anhydrous	gm.	2.0
Potasium bromide 10%	mls.	3.0
Water to	mls.	200

(ii) Barium hydroxide gm. 0.5
Borax gm. 2.4
Water to mls. 200
1% coupler in alcohol mls. 20

Example 4

Cinefilm or other photographic record is treated in a bath consisting of:

2-amino-5-diethylamino toluene HCl	gm.	1.0
Sodium sulphite anhydrous	gm.	1.6
Potassium bromide 10%	ml.	2.25
Water to	ml.	780

and was then treated with an oxidizing bath of potassium ferricyanide solution containing barium chloride and followed in turn by a bath prepared by mixing immediately before use 120 mls. of a 30% sodium carbonate cryst. solution and 100 mls. of a solution of 8 gms. of 2:4-dichlor-1-naphthol in 1 litre of alcohol.

In this example, the potassium ferricyanide is used for the oxidizing action on the aromatic diamine, in accordance with the process of my application Serial Number 580,327 and the barium chloride is used to precipitate the sulphite.

Example 5

(*a*) A photographic film employing a sensitive emulsion layer prepared from unhardened gelatine and silver salts and containing a non-actinic dyestuff such as tartrazine is exposed through the transparent support to a negative illuminated

with blue light. The film is then developed in the following bath which is fairly stable to oxidation by the air:

Pyrogallol	gms.	4.0
Potassium bromide 10% solution	mls.	8.0
Ammonium chloride	gm.	0.8
Sodium sulphite anhydrous	gms.	8.0
Sodium hydroxide 10% solution	mls.	20.0
Water	mls.	500

After two minutes' treatment the film is washed in cold water and then subjected to treatment with hot water at 130° F. This leaves little or no image in the form of a gelatine relief.

(*b*) By adding 8 gms. anhydrous calcium chloride to the above developer before use a satisfactory relief image is obtained.

By the term "sulphite" as used herein is meant any of the metabisulphites, bisulphites and neutral sulphites.

I claim:

1. In a process of photographic development of a silver salt in which in addition to the silver image there is also produced a secondary image derived from the oxidation products of the developing agent, and for which development there is employed an aqueous solution of a developing agent which prior to use contains a sulphite as preservative, the step of inhibiting the effect of said sulphite during development proper, by adding to said solution immediately before any substantial development has begun a water soluble compound of an alkaline earth metal capable of precipitating said sulphite, in an amount sufficient to bind substantially the whole of said sulphite to form a compound which is innocuous to said development.

2. Process according to claim 1 wherein said compound is calcium chloride.

3. Process according to claim 1 wherein said compound is barium chloride.

4. Process according to claim 1 wherein said compound is barium hydroxide.

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