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COMPLETE SPECIFICATION

Rapid Processing of Exposed Photographic Materials

America

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, 343 State Street, Rochester 4, New York, United States of America (Assignees of JOHN BLACKMER and HOWARD WALTER VOGT) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to photography, and more particularly to the processing of exposed sensitive photographic materials particularly colour photographic films and papers.

Multi-layer photographic materials used in colour photography usually contain at least three selectively sensitive emulsion layers coated on one side of a photographic support, such as film base or paper. One of the silver halide emulsions is usually sensitised to the red region of the spectrum, another to the green and the third to the blue region of the spectrum. In colour materials for reversal processing, there is usually a yellow filter layer between the support and the conventional uppermost blue-sensitive layer. The red-and green-sensitive layers generally lie between the yellow filter layer and the support. Such colour materials may be designed for processing in photographic developers containing a colour coupler or colour-forming compound, which couples with the oxidation products of the colour developer to provide the desired colour image. Other photographic materials are designed in such a fashion that the coupler is incorporated in the silver halide emulsion layer itself, or in a layer contiguous thereto. Such materials are well known to those skilled in the art, and it is to be understood that the present invention is mainly concerned with colour photographic materials which are

designed to be processed in colour developers containing the couplers and with colour materials which contain the couplers in the silver halide emulsions, or in layers contiguous thereto. Multi-layer materials of the type which can be employed in the present invention have been previously described in the prior art, such as Specifications Nos. 507,841 and 541,589.

It is known that photographic silver halide emulsions can be processed at elevated temperatures, thereby materially shortening the processing time. However, as the temperature of the processing solutions is raised, the photographic layers conventionally used suffer the serious disadvantage of softening, which causes offsetting of the layers and reticulation from the supporting surface, such as film or paper. Attempts have been made to overcome this softening difficulty by treatment of the photographic material before processing with an aqueous solution containing a hardener for the conventional hydrophilic colloid layers which generally contain gelatin or some similar colloidal binder. Aldehydes, such as formaldehyde, glyoxal, succinaldehyde, and glutaraldehyde, have been proposed for this purpose, but it has been found that even small amounts of these aldehydes will carry through into one or more of the colour developers and react with the colour couplers, so causing serious difficulties.

The present invention enables high temperature processing of exposed photographic materials, particularly colour materials, to be carried out while reducing or avoiding the difficulties referred to above.

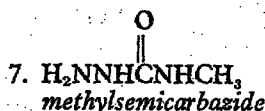
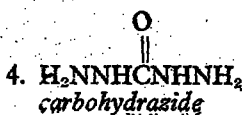
According to the present invention there is provided a method of processing exposed sensitive photographic silver halide materials which comprise a support bearing at least one layer of a photographic silver halide

[Price 4s. 6d.]

emulsion in a colloidal binder, which method comprises treating the exposed material with an aldehyde hardening agent, then treating the material with an aqueous solution of an amine compound containing a —NH_2 group having attached thereto a —NHCO— , —CONH— , —NH—C(=NH)— , —OH or —NH_2 group to remove substantially all free aldehyde from the binder, and then treating the material with an aqueous alkaline photographic silver halide developer to develop a silver or silver-plus-dye image in the exposed layer.

By this method, little or no hardening agent is carried through into one of the subsequent processing baths, such as the colour developer, where the hardening agent has deleterious side reactions leading to the formation of sludge and scum. Using this technique, it has been found possible to shorten the processing time of a conventional incorporated coupler film from approximately 52 minutes by conventional processing to about 19 minutes, while providing quality substantially equal to that obtainable using the longer processing time.

The primary amine compound employed in the process contains in addition to the —NH_2 group, a hydroxy group, a carbonyl group, or an amino group, which may have a substituent thereon. The concentration of the amine compound in the pre-bath can be varied, depending upon the amount of aldehyde which is found to carry over from the aldehyde hardening bath. In general, we have found that from 1 gram to 100 grams per litre of amine compound is sufficient to remove substantially all traces of aldehyde from the emulsion layers, so that aldehyde is not released into one of the subsequent processing baths. The amine compounds useful in the present invention, can be employed in the form of their free bases, or they can be employed in the form of their water-soluble acid addition salts, such as the hydrochloride, sulphate or phosphate. Amine compounds which can be usefully employed include the following:



In preparing the amine-containing prebath compositions useful in the present invention, it is the usual practice to dissolve one of the amine compounds in water, and then adjust the pH of the treating solution so that a pH within the range of 4.5 to 8.0 is obtained. Improved reaction of the amine compound with the aldehyde contaminants in the emulsion layers generally occurs more rapidly at a pH below 8.0. Higher pH levels can sometimes be used, although prolonged contact times may be required in order to compensate for the lower rate of reaction.

The most advantageous concentration of amine compound for a particular processing run can be determined by developing a series of test strips of photographic multi-layer elements wherein the concentration of the amine compound, as well as the concentration of the aldehyde in the hardening bath, are varied. The rate of reactivity of the amine-containing composition can be varied by variation of the pH as mentioned above. Advantageously, the pH can be varied by the addition of an alkaline solution, such as one containing sodium carbonate, potassium carbonate or sodium hydroxide, or by the addition of an aqueous acidic solution, such as a solution of acetic acid, hydrochloric acid or sulphuric acid. If desired, a buffer, such as sodium acetate, can be added to maintain the pH at a relatively constant level.

The photosensitive layers present in the photographic material processed according to the invention can contain any of the conventional silver halides as the photosensitive material, and it is to be understood that the present invention is not restricted by the chemical nature of these ingredients. Silver halide emulsions, such as silver chloride and silver bromide, can be usefully employed, although other silver halide emulsions may be employed with equal advantage. Any

of the conventional photographic supports such as glass, paper and cellulose ester film, can be used to serve as a carrier for the silver halide films.

5 The concentration of aldehyde in the aldehyde hardening bath can be varied as desired, depending upon the processing temperature and other conditions. Sufficient aldehyde is generally employed to prevent any substantial softening during later treatment with processing baths, any or all of which may be at elevated temperatures lying between about 85° F. and 150° F. The concentration of aldehyde will obviously depend upon the hardening property of the particular aldehyde employed, since some aldehydes are more reactive than others with a particular hydrophilic colloid, such as gelatin or polyvinyl alcohol.

20 The process of the invention can be used in the treatment of photographic colour elements designed for reversal colour processing, or in the processing of negative colour materials, or colour print materials. The essential feature of the invention is the use of an aqueous solution containing an amine compound of the above type after treatment of the photographic element with an aldehyde hardening bath, but prior to photographic development. This technique avoids substantial carryover of any aldehyde compound into one of the subsequent treating baths where its presence might cause deleterious effects. Washing with water following an aldehyde hardening bath does not remove sufficient aldehyde to prevent the difficulties which have been mentioned above. However, simple treatment with an aqueous solution of one of the amine compounds of the invention removes the aldehyde and even reduces the number of washing steps with water which have been previously employed in commercial processing of many photographic elements. If the concentration of amine compound is relatively high so that some of this compound carries over into one of the subsequent treating baths, this does not cause any serious difficulties. It has been found that many of these compounds have useful properties even in the subsequent treating baths. For example, where 20 grams per litre of succinaldehyde were employed in a hardening bath

to permit high temperature processing, it was found that the useful concentration of hydroxylamine (or a salt thereof) should be about 50 grams per litre, although higher amounts had no deleterious effect upon photographic quality.

Following treatment of the hardened element in the prebath, the material can thereafter be processed in a normal sequence using conventional processing solutions and techniques, or in other cases, the process can be adapted to other processing techniques, such as surface-layer processing of the type described in our copending Application No. 4861/62 (Serial No. 990,183).

The following example illustrates the present invention.

EXAMPLE

A three-colour-silver bromoiodide film, wherein gelatin was employed as the hydrophilic colloid and where cyan, magenta and yellow colour formers of the type described in Specification No. 541,589 were respectively incorporated in the emulsions, was exposed for 1/50 second to a 500-watt tungsten lamp, adjusted to a colour temperature of 6100° K., in an intensity scale sensitometer. The exposed strip was then treated for 2 minutes in a hardening bath at 100° F. having the following composition:

Succinaldehyde	-	-	-	10 grams
Sodium acetate	-	-	-	10 "
Water to make	-	-	-	1 litre

Without any intermediate water wash, the film was immersed for 30 seconds at 100° F. in an amine-containing bath having the following composition:

Sodium hexametaphosphate	0.5 gram
Hydroxylamine	25 "
Sodium bromide	1.0 "
Sodium sulphate anhydrous	50 "
Water to make	1 litre

The treated film was then developed for 3 minutes at 100° F. in a black-and-white negative developer, such as one having the following composition:

Water, 90° F. (32° C.)	-	-	-	-	1.0 litre
Sodium hexametaphosphate	-	-	-	-	2.0 grams
N-methyl-p-aminophenol sulphate	-	-	-	-	6.0 "
Sodium sulphite, desiccated	-	-	-	-	50.0 "
Hydroquinone	-	-	-	-	6.0 "
Sodium carbonate, monohydrate	-	-	-	-	35.0 "
Potassium bromide	-	-	-	-	2.0 "
Sodium thiocyanate	-	-	-	-	1.5 "
6.5% aqueous solution of 6-nitrobenzimidazole nitrate	-	-	-	-	12.0 ccs.
0.1% aqueous solution of potassium iodide	-	-	-	-	10.0 "

At this point it was possible to omit the conventional water wash and first-hardener treatment and to proceed with treatment for 30 seconds in an acid rinse bath having the following formula:

Acid Rinse	
Water - - - -	800 mls.
Glacial Acetic Acid - -	30.0 "
Sodium Hydroxide - -	1.75 grams
Water to - - - -	1 litre
pH at 80° F - - - -	3.8 ± .40

The film was then washed for 30 seconds in water at 100° F. and might then be given either a flash exposure to strong white light or a chemical exposure in a reducing bath, such as aqueous alkaline bath containing potassium borohydride. (See Specification No. 904,462) The film was then developed for 3 minutes at 100° F. in a colour developer having the following formula:

Water, 70° to 80° F. (21° to 27° C.)	1.0 litre
Benzyl alcohol - - - -	6.0 ccs.
Sodium hexametaphosphate - - - -	2.0 grams
Sodium sulphite, desiccated - - - -	5.0 "
Trisodium phosphate - - - -	40.0 "
Potassium bromide - - - -	0.25 "
0.1% aqueous solution of potassium iodide	10.0 ccs.
Sodium hydroxide - - - -	6.5 grams
4 - amino - N - (β - methanesulphon-	
amidoethyl) - m - toluidinesesquisulphate	
monohydrate - - - -	11.33 grams
Ethylenediamine sulphate - - - -	7.8 "
Citrazinic acid (2,6-dihydroxyisonicotinic	
acid) - - - -	1.5 "

At this point it was possible to omit the conventional water wash and second hardener treatments. The film was then treated for 30 seconds at 100° F. in an acid rinse bath of the type illustrated above. The film was then washed for 1 minute in water at 100° F. and then treated for 90 seconds at 100° F. in a bleach bath having the following composition:

Sodium ferricyanide - -	60.0 grams
Sodium bromide - -	15.0 "
Sodium hypophosphate	
(10H ₂ O) - - - -	17.6 "
Sodium hydroxide - -	3.5 "
Sodium thiocyanate - -	5.0 "
Water to - - - -	1 litre

The film was treated for 1 minute in a fixing bath having the following composition:

Water 80° F. (27° C.) -	1.0 litre
Sodium thiosulphate - -	95.6 grams
Sodium bisulphite - -	20.0 "

The film was then washed for 1 minute in 100° F. water and treated for 30 seconds in a stabilising bath having the following composition:

Constituent	Fresh Tank Mix
Water	800 mls.
Formalin (37.5% aqueous formaldehyde solution)	4.0 "
pH	

It was found that improved results were obtained using the process outlined above if the concentration of sodium sulphite in the negative developer was increased to a level of about 75 grams per litre instead of the 50 grams illustrated in the example. Since conventional aldehyde hardeners are eliminated in the process described in the example, it was found that undesired sludge and scum were easily avoided and that photographic quality remained at a high level. Also, since the film processed was hardened at the start of the processing operation, considerably less dirt and suspended matter were picked up from other solutions, thus making it unnecessary to use as many wash baths as would ordinarily be employed in the processing of an unhardened film. Also, since the use of a hardened material made possible processing at a much higher temperature than normal, the hydrophilic colloid layers had much less tendency to swell in the processing solutions and made it possible to dry and film in about 1/3 the normal time. The processing time was only about 19-1/2 minutes as compared with 52-1/2 minutes conventional 75° F. processing.

Other amine compounds can be employed to give the same advantages as were obtained in the above example. For instance, instead of using hydroxylamine to remove aldehyde from photographic material hardened in an aldehyde bath, carbonylhydrazide may be used. A typical formula which has been found useful for this purpose is as follows:

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Carbohydrazide - - - 5 grams
Sodium sulphate anhydrous 100 "
Water to make - - - 1 litre
pH at 80° F. - - - 6.0

5 The first developer, i.e. the black-and-white negative developer, may be a rapid developer, such as one of the MQ type, i.e. a combination of hydroquinone and Elon (p-N-methylamino-phenol sulphate) developer. "Elon" is a
10 Registered Trade Mark. Other negative developers, such as hydroquinone alone, 3-pyrazolidone developers, such as 1-phenyl-3-pyrazolidone or 4,4-dimethyl-1-phenyl-3-pyrazolidone, can also be used, if desired.

15 In order to effect colour development of the photographic materials employed in the invention, any of the conventional colour-forming developing agents, whose oxidation products couple with the conventional photographic couplers, can be employed. Especially
20 useful colour developing agents which can be employed include aromatic primary amines containing an amino (substituted or not) or hydroxyl substituent. The phenylenediamines and substituted derivatives thereof containing
25 a primary amino group have been found to provide excellent results in our invention. Typical of such colour-forming developers are the sulphonamido-substituted p-phenylenediamines described in Specification No. 651,749
30 and the substituted p-phenylenediamines described in U.S. Patent No. 2,566,271.

When practising the present invention, any of the conventional couplers as described in
35 the prior art can be used. Couplers which are particularly useful in colour developers include Couplers Nos. 1—64 listed in Specification No. 898,005. The couplers described in the same specification as Nos. 65—77 are
40 useful for inclusion in the photographic silver halide emulsion layers. Other couplers suitable for use in emulsions include those described in Specifications Nos. 660,012; 674,161; 649,660; and 595,314. Other
45 couplers which can be used in the emulsions of the present invention include acylamino-substituted couplers, such as those described in Specification No. 562,205.

WHAT WE CLAIM IS:—

50 1. A method of processing exposed sensitive photographic silver halide materials which

comprise a support bearing at least one layer of a photographic silver halide emulsion in a colloidal binder, which method comprises treating the exposed material with an aldehyde
55 hardening agent, then treating the material with an aqueous solution of an amine compound containing an —NH₂ group having attached thereto a —NHCO—, —CONH—, —NH—C(=NH)—, —OH or —NH₂ group
60 to remove substantially all free aldehyde from the binder, and then treating the material with an aqueous alkaline photographic silver halide developer to develop a silver or silver-plus-dye image in the exposed layer.

2. A method as claimed in Claim 1, in which the sensitive photographic silver halide, material comprises a support bearing three silver halide emulsion layers each sensitive to a different region of the spectrum.

3. A method as claimed in Claim 2, in which each emulsion layer contains a colour coupler for the formation of a subtractively coloured image therein.

4. A method as claimed in Claim 3, in which, after the treatment with the amine compound, the material is treated with a black-and-white developer, then the layers are individually exposed uniformly and treated with a colour developer so as to form a subtractively coloured three-colour image in the material, any or all of the baths after the treatment with the amine compound being heated to at least 85° F. to accelerate processing.

5. A method as claimed in any preceding claim, in which the amine compound is any of those hereinbefore specified.

6. A method as claimed in any preceding claim, in which the colloidal binder of the emulsion layer or layers is gelatin.

7. A method as claimed in any preceding claim, in which the aldehyde is formaldehyde or succinaldehyde.

8. A method as claimed in any preceding claim in which the solution of the amine compound is adjusted to a pH of between 4.5 and 8.0.

9. Methods of processing exposed photographic silver halide materials according to Claim 1, substantially as herein described.

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Patent Agent.

R. M.

Carbohydrazide - - - 5 grams
Sodium sulphate anhydrous 100 "
Water to make - - - 1 litre
pH at 80° F. - - - 6.0

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9. Methods of processing exposed photographic silver halide materials according to
100 Claim 1, substantially as herein described.

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