(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 559 276 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **93200538.2**

(51) Int. Cl.^{5}: **G03C 1/83**

(22) Date of filing: **25.02.93**

(30) Priority: **29.02.92 GB 9204406**
31.07.92 GB 9216330

(43) Date of publication of application:
08.09.93 Bulletin 93/36

(84) Designated Contracting States:
BE CH DE FR GB IT LI NL

(71) Applicant: **KODAK LIMITED**
Patent Department, Headstone Drive
Harrow, Middlesex HA1 4TY(GB)
(84) **GB**

(71) Applicant: **EASTMAN KODAK COMPANY**
343 State Street
Rochester, New York 14650-2201(US)
(84) **BE CH DE FR IT LI NL**

(72) Inventor: **Rogers, David Neil, c/o Kodak Limited**
Patent Department, Headstone Drive
Harrow, Middlesex, HA1 4TY(GB)
Inventor: **Higgins, John Martin, c/o Kodak Limited**
Patent Department, Headstone Drive
Harrow, Middlesex, HA1 4TY(GB)
Inventor: **Fyson, John Richard, c/o Kodak Company**
Patent Department, Headstone Drive
Harrow, Middlesex, HA1 4TY(GB)

(74) Representative: **Baron, Paul Alexander Clifford et al**
Kodak Limited Patent Department Headstone Drive
Harrow Middlesex HA1 4TY (GB)

(54) Processing photographic colour negative films.

(57) A method of reducing the chemical load on the bleach bath during the processing an imagewise exposed photographic multilayer colour negative film by using, instead of a grey silver antihalation layer, a dye-containing, silver-free layer which is destroyed or otherwise removed during photographic processing as the sole antihalation layer in the film.

EP 0 559 276 A1

This invention relates to the processing of photographic colour negative films.

In "The Theory of the Photographic Process", Ed. T. H. James, Macmillan 1977 at page 579 it states that reflections back from the support of a photographic material causes the appearance of halos around bright objects. This effect is known as halation and results generally in a loss of sharpness of the image. It further states therein that three methods can be used to reduce its effect:

(1) Coating an antihalation undercoat which is either dyed gelatin or gelatin containing grey silver (used in colour films) between the emulsion and the support;

(2) Coating the emulsion on a support that contains either dye or pigments (for example carbon); and

(3) Coating the emulsion on a transparent support that has a dyed or pigmented layer coated on the back (or opposite side) of the support.

For methods (1) and (3) it is normal to remove or destroy the colour of the antihalation layer during processing. In (2) the colour is permanent and cannot be destroyed chemically.

It is clear that it is only necessary to reduce reflected light in the spectral regions to which the emulsion(s) are sensitive. Thus, for an infra-red sensitive film for example, it is only necessary to absorb infra-red radiation in the antihalation layer. It is for this reason that many black and white materials have antihalation layers formed of coloured dyes or pigments.

Photographic colour materials which typically have emulsion layers sensitised to the red, green and blue regions of the spectrum need an antihalation layer which absorbs in all three regions. Colour films are able to use a grey metallic silver layer as an antihalation layer (type 1 above) because it will be removed during processing in the bleach and fix baths. This is convenient because silver absorbs fairly uniformly across the spectrum. All commercially available colour negative films use such a grey silver antihalation layer.

US Patent 4 092 168 discloses the use of dyes of the type used in the present invention, for use in antihalation layers in black and white photographic materials. This is said to be an improvement over the previous practice of using a mixture of dyes to allow absorption across the whole visible spectrum. The specific disclosure is of an antihalation backing layer covered with an anticurl layer. The dye is removed from the film during processing. It is noted that a grey silver antihalation layer cannot be removed from black and white materials in the bleach because the bleach bath would not only bleach the antihalation layer but also the silver image.

US Patent 4 855 221 describes the use of solid particle dispersions of certain oxonol dyes (preferred for use in the present invention) as filter layers in photographic materials. Multicolour photographic elements are mentioned but no photosensitive materials are actually exemplified.

There is constant desire to reduce the chemical load on photographic processing solutions to reduce chemical consumption and to reduce the amount of effluent which has to be safely disposed of without compromising film performance.

According to the present invention there is provided a method of processing an imagewise exposed photographic multilayer colour negative film comprising at least three silver halide differently sensitised emulsion layers having associated respectively therewith different dye image-forming couplers and having between the emulsion layers and the support a silver-containing antihalation layer, comprising at least the steps of colour development, bleaching and fixing *characterised in that* the chemical load on the bleach bath is reduced by using a dye-containing, silver-free layer which is destroyed or otherwise removed during photographic processing as the sole antihalation layer in the film.

The present invention will usually also reduce the chemical load on the fix solution as well.

The reduction in chemical load may be achieved in a number of ways. For example, the rate of replenishment of the bleach and fix baths may be reduced. Alternatively the concentration of the two baths may be reduced or the time of processing may be reduced.

The present invention has the advantage of reducing the chemical load on the bleach and usually the fix bath as well. The advantage may be taken as lower replenishment rates, lower concentrations of active ingredients, faster processing times or combinations thereof. In addition the quantity of effluent is also reduced. The presence in colour negative films of a grey silver layer (in its bleached form) can provide a catalyst for the formation of silver iodide (which is very difficult to fix out) at the latter part of the fix process thereby making the fix step take a longer time. This problem is also avoided.

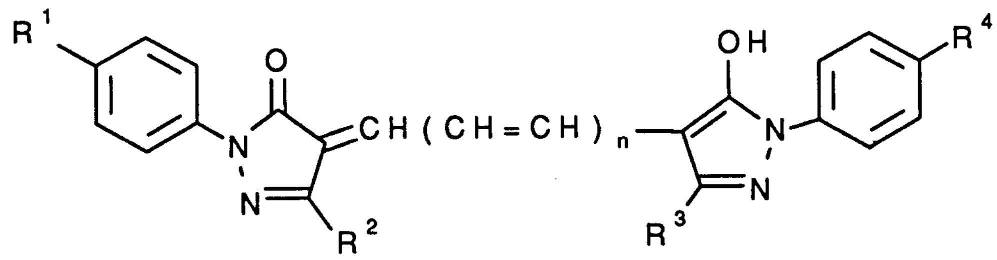
The bleach solution oxidises metallic silver to a silver salt. The oxidising (or bleaching) agent may comprise iron(III), for example in the form of an alkali metal ferricyanide, permanganate, dichromate, ferric ethylenediamine-tetraacetic acid, ferric propylenediamine-tetraacetic acid, or hydrogen peroxide. Such baths are well known and are described, for example, in "Modern Photographic Processing", Grant Haist, John Wiley, New York, and "The Theory of the Photographic Process", fourth edition, Ed. James, MacMillan.

The fixer may comprise an alkali metal or ammonium thiosulphate or thiocyanate as fixing agent or, in the case of low silver coating weight materials comprising silver chloride, and alkali metal sulphite. Again fix baths are well known and are described in "Modern Photographic Processing" above.

The bleach and the fix baths may be combined into a single bleach-fix bath and these are also described in "Modern Photographic Processing" above.

When used commercially, as is well known, processing solutions are replenished to replace active ingredients used up during processing or which are destroyed by chemical reaction either during processing or when standing idle, for example by aerial oxidation. The nature of such replenishment techniques and solutions are well understood.

The dye is preferably an oxonol dye. Such dyes are bleached by the sulphite ions in the developer solution. Preferably the dye has the general formula:

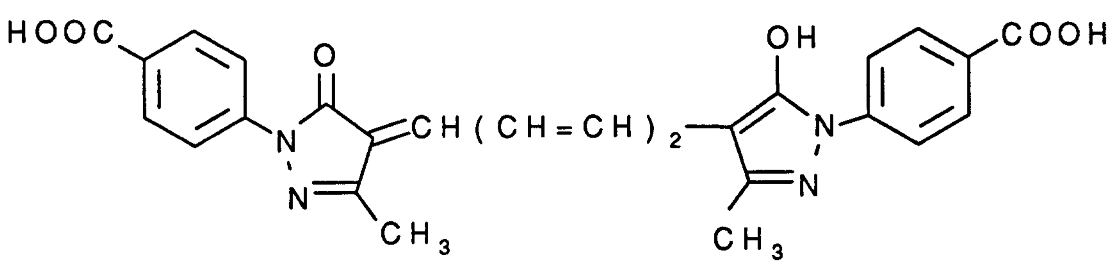


Formula I

wherein R^1 to R^4 are each individually hydrogen, halogen or an alkyl, aryl, heterocyclic, R^5X-, R^5X-NR^6-, R^5R^6N-X- any of which may be further substituted, -COOH OR SO_3H, wherein X is CO or SO_2 and R^5 and R^6 are alkyl, aryl or heterocyclic groups which can be further substituted, and

n is 0 to 3.

A specific example of the above dyes has the formula:



Formula II

The dyes of formula I and II may be coated as solutions or solid dye dispersions.

In addition to the above dyes it is also possible to use a dye which is soluble in one or more of the processing solutions used so that it is leached out of the film during processing.

The present colour films preferably comprise a yellow dye image-forming unit comprised of at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler, at least one magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler at least one cyan dye image-forming unit comprising at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, said image-forming units being carried on a support.

The couplers, emulsions, additives, supports, structure, etc of the present colour films may be any of those described in Research Disclosure Item 308119, December 1989 published by Kenneth Mason Publications, Emsworth, Hants, United Kingdom.

The invention is illustrated by the following Example.

EXAMPLE 1

A standard full colour photographic negative film was coated with modification to the anti-halation layer, which was coated on top of subbed base over which was coated the remainder of the film. The antihalation layer either contained the usual grey silver with silver levels varied, a dye of Formula II, as a replacement for the grey silver, also coated at different levels. A plain gelatin layer was also coated with each set as a control.

Strips of the coated materials were processed in the following process:

Film Development Process at 38 °C	
1. Colour developer	3.25 mins
2. Bleach	see below
3. Wash	1.5 mins
4. Fix	4.3 mins
5. Stabilise	1.0 mins

Colour developer	
Diethylenetriaminepentacetic acid	2.0 g
Sodium sulphite (anhy)	4.25 g
Potassium bromide	1.5 g
Hydroxylamine sulphate	2.0 g
Potassium carbonate	25.0 g
4-(N-ethyl-N-2-hydroxyethyl)-2-methylphenylenediamine	4.75 g
Water to	1.0 litre
pH = 10.1	

Bleach	
Potassium iron(III) 1,3-propylenediamine-tetra-acetic acid	0.11 molar
Potassium bromide	0.4 molar
Acetic acid	1.0 molar
pH adjusted to 4.75 at 25 °C	

Fixer	
Ammonium thiosulphate	120.0 g
Sodium sulphite (anhy)	20.0 g
Potassium metabisulphite	20.0 g
Water to	1.0 litre

Stabiliser	
Formaldehyde (36% soln)	6.0 ml
Water to	1.0 litre

The bleaching time was monitored by measuring the infra-red density of the film continuously while in the bleach. The time at which the density had ceased to change was taken as the bleach time.

Table 1 shows the bleaching times and sharpnesses, measured as AMT numbers (the bigger, the sharper) of the coatings in both 35mm and Disc film formats.

Table 1

AHU type	Silver or Dye Laydown (g/m^{-2})	Bleach Time (secs)	Fix Time (secs)	AMT 35mm	Disc
Gel	-	72±5	42	91.8	82.9
Gel + Ag	0.1	77±5	44	94.3	85.7
	0.2	80±5	46	94.1	85.1
	0.3	99±5	47	93.6	84.8
	0.4	140±5	50	92.9	83.9
Gel	-	61±5	38	91.1	82.6
Gel + Dye	0.02	62±5	37	93.3	84.8
	0.04	50±5	39	93.2	84.6
	0.08	58±5	40	93.9	85.4
	0.10	56±5	39		

These results indicate that both the silver and dye antihalation layers give sharper images as measured using the AMT metric compared to the pure gelatin control layers. However the use of silver increases both the bleaching and fixing times, whereas the use of dye makes very little or no impact on the bleaching time, in most cases reducing it. Using the dye can therefore give sharp images without increased process time. The consumption of less bleaching and fixing agent per film will also reduce effluent levels.

EXAMPLE 2

Two coatings of a ISO400 speed film were made containing 2.5g/m^2 imaging silver in the each of the blue, green and red sensitive layers. Each film had a yellow silver filter layer with a coated laydown of 0.2g/m^2. One of the films was coated with a grey silver AHU(comparison) and the other a dye layer coated at 0.04g/m^2 dye as described in Example 1. These films were processed in a processing machine with the following process times and temperatures:

	Time	Temperature
Develop	3.25 mins	37.8 °C
Bleach	3.33 mins	38.0 °C
Fixer	1.50 mins	38.0 °C
Wash	3.00 mins	38.0 °C
Stabiliser	1.00 mins	38.0 °C
Dry	2.00 mins	40.0 °C

The tanks of the processor were filled with the solutions described in Example 1. Replenishers were made up as described below and the rate of replenishment of the bleach and fix adjusted so that the bleaching and fixing were just adequate to remove the silver from the film after three tank turnovers of seasoning.

Developer Replenisher	
Diethylenetriaminepentacetic acid	2.0g
Sodium sulphite anh.	5.0g
Potassium bromide	1.0g
Hydroxylamine sulphate	2.5g
N-1-ethyl-N-2-hydroxyethyl-2-Methyl-p-phenylenediamine	5.2g
Potassium carbonate	25.0
Water to	1 litre
pH adjusted to 10.13 Replenishment rate fixed at 39mls/m	

Bleach Replenisher	
Potassium iron(III)-1,3-propylenediamine-tetracetic acid	0.15molar
Potassium bromide	0.6molar
Acetic acid	1.5molar
pH adjusted to 4.25	

Fixer Replenisher	
Ammonium thiosulphate	146g
Sodium sulphite	15g
Potassium metabisulphite	15g
Water to	1litre

Stabiliser Replenisher	
Formaldehyde (36% solution)	7.0 ml
Water to 1 litre	1.0mls
Replenisher fixed at 65ml/m	

Antihalation layer	Replenishment rates (mls/m)	
	Bleach	Fixer
Silver AHU	21.9	28.9
Dye AHU	4.9	27.6

As can be seen the resulting replenishment rates (expressed as mls per linear metre of film) can be reduced by having a dye AHU layer. This would result in a saving of over 75% iron and associated chelate in the effluent and 4% sulphur compound from the fixer.

EXAMPLE 3

Example 2 was repeated but in this instance the replenishment rates of the bleach and fixer were held at 21.9 mls/m and 28.9 mls/m respectively and the concentrations of the active ingredients in the replenishers varied until the process just remove all the silver from the films after seasoning for three tank turnovers. The results are shown in the table below.

Antihalation layer	Replenisher concentrations	
	Bleach	Fixer
Silver AHU Dye AHU	0.15 molar 0.14 molar	146g/l 140g/l

Again a saving of materials can be gained and less chemistry goes to waste.

EXAMPLE 4

The fixing rates of the two films after they had been processed through the developer and bleach as described in Example 2 were measured in an all sodium fixer of the following constitution:

Sodium thiosulphate pentahydrate	200g
Sodium sulphite	20g
Sodium metabisulphite	20g
Water to	1litre

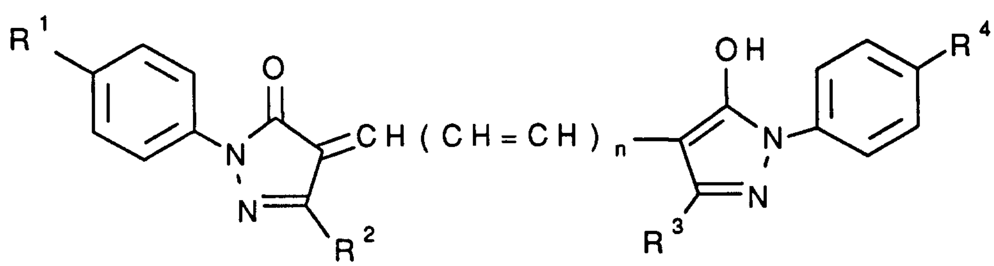
The fixing time for the film with the silver AHU was 190s and that with the dye AHU 170s. This shows a benefit in fixing time of a dye AHU layer in an all sodium fixer.

Claims

1. A method of processing an imagewise exposed photographic multilayer colour negative film comprising at least three silver halide differently sensitised emulsion layers having associated respectively therewith different dye image-forming couplers and having between the emulsion layers and the support a silver-containing antihalation layer, comprising at least the steps of colour development, bleaching and fixing ***characterised in that*** the chemical load on the bleach bath is reduced by using a dye-containing, silver-free layer which is destroyed or otherwise removed during photographic processing as the sole antihalation layer in the film.

2. A method as claimed in claim 1 wherein the dye is an oxonol dye.

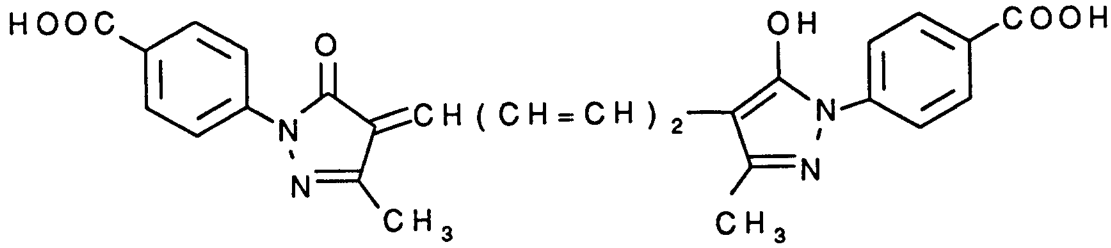
3. A method as claimed in claim 1 or 2 wherein the dye has the general formula:



Formula (I)

wherein R^1 to R^4 are each individually hydrogen, halogen or an alkyl, aryl, heterocyclic, R^5X-, R^5X-NR^6-, R^5R^6N-X- any of which may be further substituted, -COOH OR SO_3H, wherein X is CO or SO_2 and
R^5 and R^6 are alkyl, aryl or heterocyclic groups which can be further substituted and
n is 0 to 3.

4. A method as claimed in any of claims 1 to 3 wherein the dye has the general formula:



Formula (II)

5. A method as claimed in any of claims 1 to 3 wherein the dye is present as a solid particle dispersion.

6. A method as claimed in any of claims 1 to 5 wherein the hydrophilic colloid comprises gelatin or a derivative thereof.

7. A method as claimed in any of claims 1 to 6 in which the film comprises a yellow dye image-forming unit comprised of at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler, at least one magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler at least one cyan dye image-forming unit comprising at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, said image-forming units being carried on a support.

8. A method as claimed in any of claims 1-7 in which the chemical load on the fixer solution is also reduced.

9. A method as claimed in any of claims 1-8 in which the chemical load is reduced by reducing the rate of replenishment of the bleach and optionally the fix solution.

10. A method as claimed in any of claims 1-8 in which the chemical load is reduced by reducing the concentration of the bleach and optionally the fix solution.

11. A method as claimed in any of claims 1-8 in which the chemical load is reduced by reducing the processing time in the bleach and optionally fix solutions.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 20 0538

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 316 013 (FUJI PHOTO FILM CO., LTD) 17 May 1989 * page 5, line 20 - page 5, line 54 * *page 10, compound 21* * example 2 *	1-3,5-11	G03C1/83
Y	* example 2 *	4	

Y	EP-A-0 299 435 (EASTMAN KODAK COMPANY) 18 January 1989 * claim 1 *	4	
D	& US-A-4 855 221		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	16 JUNE 1993	MARKOWSKI V.F.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document