

## PATENT SPECIFICATION

454,498

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Complete Specification Left: March 20, 1936.

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## PROVISIONAL SPECIFICATION

## Improvements in Colour Photography

We, KODAK LIMITED, a British Company, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention which has been communicated to us by Eastman Kodak Company, a body corporate organised according to the laws of the State of New York, United States of America, of 343, State Street, Rochester, New York, United States of America, to be as follows:—

This invention relates to photographic processes and more particularly those adapted to colour motion pictures.

The Parent Specification No. 18934/34 (427,518) relates to the processing of photographic record elements having a plurality of layers containing different colour sensation records on a single support and in particular to improvements in the type of processing in which the action of a bleaching bath or a developing bath, as the case may be, is to be restricted to an upper layer leaving a lower layer materially unaffected thereby. In carrying out such a process the action of the processing bath has to be arrested before it has substantially penetrated a lower layer and materially affected the image therein.

According to one feature of that invention, control of the diffusion of the bleaching bath or the developing bath, as the case may be, is facilitated by the presence therein of a water-soluble loading agent. Sodium sulphate is given as an example of a loading agent for a hydroquinone developing bath and for a ferricyanide bleaching bath. A water-soluble organic liquid such as methanol is given as an example of a loading agent for a chromic acid-bromide bleach bath for a colour developed layer.

According to one feature of improvement in or modification of the invention claimed in application No. 18934/34 (427,518) the loading agent is sugar or sodium chloride or a mixture thereof.

According to another feature of improvement in or modification of the invention claimed in application No. 18934/34 (427,518) the loading agent

comprises one or more of the water-soluble higher alcohols.

According to another feature of improvement in or modification of the invention claimed in application No. 18934/34 (427,518) the loading agent comprises one or more of the water-soluble ketones.

According to another feature of improvement in or modification of the invention claimed in application No. 18934/34 (427,518) the loading agent comprises one or more of the water-soluble alkyl or alkoxy amines, acylated or not.

According to another feature of improvement in or modification of the invention claimed in application No. 18934/34 (427,518) the loading agent comprises one or more of the polyhydric alcohols such as the glycols and glycerol.

According to another feature of improvement in or modification of the invention claimed in application No. 18934/34 (427,518) the loading agent comprises one or more colloids such as gelatine or gum arabic or mixtures thereof.

The materials which are employed as loading agents may be of two general types which we believe to act as follows: The first type acts by causing a repulsion between gelatine and the material added, a material of this type being alcohol. The second type acts at least partly by increasing the viscosity of the treatment bath, materials of this type being sugars or albumen or casein in the presence of alkali. These two types of loading agents possess the common property of producing an anti-swelling effect. Some of the loading agents may act in both ways to produce an anti-swelling effect.

Our invention is more clearly illustrated by the following examples of treatment baths capable of chemically transforming a photographic image, in which a loading agent is added to the bath. The following formula illustrates a bleach bath which may be used to decolourize a dye in various types of multi-layer films,

methyl alcohol, sugar and salt being used as the loading agents:

FORMULA I.

	(Quinone	-	-	-	5 g.	
5	A	(Methyl Alcohol	-	-	1000 cc.	
		(HCl	-	-	5 cc.	
		(Sugar	-	-	300 g.	
	B	(Sodium Chloride	-	-	50 g.	
		(Water	-	-	250 cc.	

10 In using this bleach bath, B is added to A.

15 A stop bath suitable for terminating the action of this bleach bath comprises a 2% solution of sodium bicarbonate in water. The film is treated in this bath immediately after being removed from the bleach bath and the bleaching action is thereby terminated.

20 The photographic record element which is treated and which may be a film such as a motion picture film, may have two, three or more layers on the same side of the support.

25 In our co-pending application, Nos. 440,032, 440,089 and 447,092, we have disclosed processes in which the images of a multi-layer film are coloured by a dye-formation process. A dye is formed and deposited in the gelatine at the places where an image is formed on development, this dye-formation involving the combination of the oxidation product of the developer with a dye-forming compound present in the developer solution. This process may be applied to reversed images or the film may be developed as a negative, and positives printed from it.

30 As applied to reversal processes, the essential steps involved in the process are as follows: The film containing the negative image is developed in an ordinary metol - hydroquinone type of developer, bleached to remove the silver images thereby formed, and exposed to light to develop the complementary silver bromide images. The film is then immersed in a colour-forming developer and monochrome-dye images formed in each of the layers. The film is then fixed to remove any residual silver halide which may be present, and dried. The next step, which is a critical one in the process, involves bleaching the outer layers or layer, but not the innermost layer to decolorize the dye and convert the silver in the outer layer or layers to silver halide. A loading agent is used in this bleach bath to control the depth and time of penetration of the bath. In order to terminate the action of this bleach bath at the desired time, the film

is then immediately immersed in a stop bath which in the case of an acid bleach may be a mild alkali such as sodium bicarbonate. The outer emulsion layer or in the case of a three-layer film the two outer layers are then redeveloped by immersion in a colour-forming developer, which forms dye images of another colour in those layers by development of the silver halide and formation of a dye at the image portions. The outer layer is then bleached as before in a bleach bath containing a loading agent and the film again immediately subjected to a stop bath such as sodium bicarbonate or sodium bisulphite. The outer layer is then finally colour-developed to a third colour, and the silver in the images removed from the three layers. The bleach baths used to decolorize the dye and convert the silver to silver halide in this process may have one of the following formulæ in which isopropyl alcohol, glycerine or ethylene glycol act as the loading agents:

FORMULA II.

	Glycerine	-	-	-	500 cc.	
	Iso-propyl alcohol	-	-	-	1000 cc.	90
	Water	-	-	-	75 cc.	
	Quinone	-	-	-	5 g.	
	HCl (concentrated)	-	-	-	20 cc.	

FORMULA III.

	Glycerine	-	-	-	500 cc.	95
	Iso-propyl alcohol	-	-	-	1000 cc.	
	Quinone	-	-	-	5 g.	
	HCl (concentrated)	-	-	-	50 cc.	

FORMULA IV.

	Ethylene Glycol	-	-	-	500 cc.	100
	Quinone	-	-	-	5 g.	
	Water	-	-	-	200 cc.	
	HCl (concentrated)	-	-	-	20 cc.	

A stop bath suitable for terminating the action of each of these bleach baths may have the following formula in which sodium bicarbonate acts as the stopping or terminating agent, the bath also containing iso-propyl alcohol and glycerine:

FORMULA V.

	Sodium bicarbonate	-	-	-	15 g.	110
	Iso-propyl Alcohol	-	-	-	1000 cc.	
	Glycerine	-	-	-	1000 cc.	
	Water	-	-	-	1000 cc.	

The invention may be applied to the selective development of the layers of a multi-layer film containing colour separation latent images which is subjected to a differential development. The outer image only is developed and the image in the inner layer is then coloured by a

colour development procedure. Developers suitable for this differential development are the following:

## FORMULA VI.

5	Hydroquinone	-	-	12.5 g.
	Sodium sulphite	-	-	19.0 g.
	KOH	-	-	41.0 g.
	Na <sub>2</sub> SO <sub>4</sub>	-	-	200.0 g.
	Water to	-	-	1 litre.

## FORMULA VII.

10	Amidol	-	-	50 g.
	Sodium sulphite	-	-	100 g.
	Na <sub>2</sub> SO <sub>4</sub>	-	-	200 g.
	Water to	-	-	1 litre.

15 A suitable stop bath for terminating the action of these developer baths may have the following formula:

## FORMULA VIII.

20	Sodium bisulphite	-	-	50 g.
	Glacial acetic acid	-	-	30 cc.
	Water to	-	-	1 litre.

The following stop bath may be used with these developer baths as an alternative formula:

## FORMULA IX.

25	Glacial acetic acid	-	-	50 cc.
	Water	-	-	1 litre.

Each of these baths should be cooled to a temperature of 0° C. to 5° C. for use.

30 Hydroquinone and its derivatives are very sensitive to temperature and are relatively inactive at low temperatures. For this reason the use of these stop baths at a low temperature brings about an immediate cessation of the developing action.

A 3% acetic acid solution may also be used as a stop bath for these developers.

40 The methods of control indicated above, additional to the presence of the loading agent, are as follows:—

1. the action of the processing bath is rapidly interrupted or terminated by means of a stop bath;

45 2. the layer is in a thoroughly dry condition when the processing bath is applied;

3. the several layers of the film are separated by inert layers;

50 4. the temperature of the photographic element is suddenly and materially lowered. This step is more effective with certain baths than with others;

55 5. the layers may be somewhat hardened.

60 It is to be understood that these various means, while useful independently, are of greatest utility when used together, although all do not need to be used since certain of the steps are particularly use-

ful in combination with certain other control means. The last mentioned two methods are of definitely minor importance.

65 Preferably the photographic material used is one in which two, three or more layers of differentially colour sensitized material are coated one upon another with intervening layers of inert material. Ordinarily gelatine is the material of all the layers, and all have the same permeability so that, unless otherwise controlled, the baths have the same diffusing properties as to all the layers.

70 As examples of the loading agents which we may employ, various compounds may be mentioned. Among the organic solvents the higher alcohols have been found suitable. These include the primary, secondary, and tertiary forms such as normal propyl and iso-propyl alcohols, the butyl alcohols and amyl alcohol. The ketones may be used, such as acetone and its homologues.

75 Amines may be used such as methyl, ethyl and propyl, and higher amines; tri-ethanol amine and other alkyl amines; acetylated alkyl amines such as N-methyl acetamide and acetamide. Among other substances which may be used are ethylene and propylene glycol, dihydroxyethylether, or aqueous solutions of gelatine, glue or gums such as gum arabic, dextrine, gum tragacanth, starches including flour and arrowroot and solutions of various solids such as sugar, and sodium chloride, potassium sulphate or other substances or salts or mixtures thereof which are inert to the photographic process and whose solutions swell gelatine less than does plain water.

80 These compounds may be used alone or two or more may be used together as loading agents. We also include the use of substances which are soluble in mixtures of water and organic solvents. Various proportions may be used depending on the degree of retarding action desired. It has been found that a dye 85 bleaching bath, for example, which penetrates a gelatin layer of .0005 inches thickness in one or two seconds can be so retarded that it will penetrate the same thickness of gelatin in four or five 90 minutes by the addition of 75% of a loading agent to the solution. The time of penetration may be decreased or increased as desired by the addition of more or less of loading agent. 95 100 105 110 115 120

Dated this 28th day of March, 1935.  
W. P. THOMPSON & CO.,  
12, Church Street, Liverpool, 1,  
Chartered Patent Agents.

## COMPLETE SPECIFICATION

**Improvements in Colour Photography**

We, KODAK LIMITED, a British Company, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention which has been  
 5 communicated to us by Eastman Kodak Company, a body corporate organised according to the laws of the State of New York, United States of America, of 343, State Street, Rochester, New York,  
 10 United States of America, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to colour photographic processes and more particularly those adapted to colour motion pictures.

The Patent Specification No. 427,518 relates to the processing of photographic record elements having a plurality of  
 20 layers containing different colour sensation records on a single support and in particular to improvements in the type of processing in which the action of a bleaching bath or a developing bath, as  
 25 the case may be, is to be restricted to an upper layer leaving a lower layer materially unaffected thereby. In carrying out such a process the action of the processing bath has to be arrested before  
 30 it has substantially penetrated a lower layer and materially affected the image therein.

According to one feature of that invention, control of the diffusion of the  
 35 bleaching bath or the developing bath, as the case may be, is facilitated by the presence therein of a water-soluble loading agent. In that specification we have claimed the employment of sodium sulphate  
 40 as a loading agent and have given examples of its use in a hydroquinone developing bath and in a ferricyanide bleaching bath: we have also claimed the employment of a water-soluble organic  
 45 liquid such as methanol as a loading agent and have given an example of the use of methanol for this purpose in a chromic acid-bromide bleach bath for a colour developed layer. These examples  
 50 also appear in the specification of Patent No. 427,472 as open to inspection before the date of the present application.

The present invention relates to colour photographic processes of the type referred to in the parent patent and is concerned with the employment of various  
 55 loading agents which have been found effective in carrying out the method claimed in the parent specification.

60 According to one feature of improve-

ment in or modification of the invention claimed in specification No. 427,518 the loading agent is sugar or sodium chloride or a mixture thereof.

According to another feature of improvement in or modification of the invention claimed in Specification No. 427,518 the loading agent comprises one or more of the water-soluble higher  
 70 alcohols, i.e. containing more than two carbon atoms.

According to another feature of improvement in or modification of the invention claimed in Specification No. 427,518 the loading agent comprises one  
 75 or more of the water-soluble ketones.

According to another feature of improvement in or modification of the invention claimed in Specification No. 427,518 the loading agent comprises one  
 80 or more of the water-soluble alkyl or alkoxy amines, acylated or not.

According to another feature of improvement in or modification of the invention claimed in Specification No. 427,518 the loading agent comprises one  
 85 or more of the polyhydric alcohols such as the glycols or glycerol.

According to another feature of improvement in or modification of the invention claimed in Specification No. 427,518 the loading agent comprises one  
 90 or more colloids such as gelatine or gum arabic or mixtures thereof.

According to a further feature of improvement in or modification of the invention claimed in Specification No. 427,518 the loading agent comprises an inert salt, other than sodium sulphate,  
 100 which can be employed in high concentration in the bleaching bath, such as potassium sulphate or sodium chloride.

The materials which are employed as loading agents according to the present invention possess the common property of  
 105 producing an anti-swelling effect upon the gelatine of the photographic elements. It is believed that this effect is brought about by two distinct actions. The first of these actions is the causing of a re-  
 110 pellancy between gelatine and the material added, materials producing this type being alcohol and salts. The present invention does not however, include the employment of sodium sulphate nor the  
 115 lower alcohols methanol and ethanol as loading agents. The second of these actions is the increasing of the viscosity of the treatment bath, materials producing this being sugars or albumen or  
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casein in the presence of alkali. Some of the loading agents probably act in both ways to produce an anti-swelling effect.

Our invention is more clearly illustrated by the following examples of bleaching developing baths in which a loading agent is added to the bath. The following formula illustrates a bleach bath which may be used to bleach a silver image record in an upper layer of a multi-layer film, methyl alcohol, sugar and salt being used as the loading agents:

## FORMULA I.

15	A	Quinone	-	-	5 g.
		Methyl Alcohol	-	-	1000 cc.
		HCl	-	-	5 cc.
B	B	Sugar	-	-	300 g.
		Sodium Chloride	-	-	50 g.
		Water	-	-	250 cc.

In using this bleach bath, B is added to A.

This bleach bath can also be used to bleach a colour developed record in an upper layer of a multi-layer film as stated in our co-pending application No. 9870/35 (Serial No. 454,499).

A stop bath suitable for terminating the action of this bleach bath comprises a 2% solution of sodium bi-carbonate in water. The film is treated in this bath immediately after being removed from the bleach bath and the bleaching action is thereby terminated.

The photographic record element which is treated and which may be a film such as a motion picture film, may have two, three or more layers on the same side of the support.

In our co-pending application Nos. 440,032, 440,089 and 447,092, we have disclosed processes in which the images of a multi-layer film are coloured by colour development. A dye is formed and deposited in the gelatine at the places where an image is formed on development, this dye-formation involving the combination of the oxidation product of the developer with a dye-forming compound present in the developer solution. This process may be applied to reversed images or the film may be developed as a negative and positives printed from it.

As supplied to reversal processes, the essential steps involved in the preferred form of such process as described in specification No. 440,032 are as follows: The film containing the negative image is developed in an ordinary metolhydroquinone type of a developer, bleached to remove the silver images thereby formed, and (if necessary) exposed to light to render the complementary silver bromide

images developable. The film is then immersed in a colour-forming developer and monochrome-dye images formed in each of the layers. The film is then fixed to remove any residual silver halide which may be present, and dried. The next step, which is a critical one in the process, involves bleaching the outer layers or layer, but not the innermost layer to decolorize the dye and convert the silver in the outer layer or layers to silver halide. A loading agent is used in this bleach bath to increase the time of penetration of the bath and thus facilitate control in restriction of the depth of penetration. In order to terminate the action of this bleach bath at the desired time, the film is then immediately immersed in a stop bath which in the case of an acid bleach may be a mild alkali such as sodium bicarbonate. The outer emulsion layer or in the case of a three-layer film the two outer layers are then redeveloped by immersion in a colour-forming developer, which forms dye images of another colour in those layers by development of the silver halide and formation of a dye at the image portions. The outer layer is then bleached as before in a bleach bath containing a loading agent and the film again immediately subjected to a stop bath such as sodium bicarbonate or sodium bisulphite. The outer layer is then finally colour-developed to a third colour, and the silver in the images removed from the three layers. The bleach baths used to decolorize the dye and convert the silver to silver halide in this process may have one of the following formulae in which isopropyl alcohol, glycerine or ethylene glycol act as the loading agents:

## FORMULA II.

Glycerine	-	-	500 cc.
Iso-propyl alcohol	-	-	1000 cc.
Water	-	-	75 cc.
Quinone	-	-	5 g.
HCl (concentrated)	-	-	20 cc.

## FORMULA III.

Glycerine	-	-	500 cc.
Iso-propyl alcohol	-	-	1000 cc.
Quinone	-	-	5 g.
HCl (concentrated)	-	-	50 cc.

## FORMULA IV.

Ethylene Glycol	-	-	500 cc.
Quinone	-	-	5 g.
Water	-	-	200 cc.
HCl (concentrated)	-	-	20 cc.

A stop bath suitable for terminating the action of each of these bleach baths may have the following formula in which sodium bicarbonate acts as the stopping

or terminating agent, the bath also containing iso-propyl alcohol and glycerine:

## FORMULA V.

	Sodium bicarbonate	-	-	15 g.
5	Iso-propyl Alcohol	-	-	1000 cc.
	Glycerine	-	-	1000 cc.
	Water	-	-	1000 cc.

The invention may be applied to the selective development of the layers of a multi-layer film containing colour separation latent images which is subjected to a differential development. The outer image only is developed and the image in the inner layer is then coloured by a colour development procedure. Developers suitable for this differential development are the following:

## FORMULA VI.

	Hydroquinone	-	-	12.5 g.
20	Sodium sulphite	-	-	19.0 g.
	KOH	-	-	41.0 g.
	Na <sub>2</sub> SO <sub>4</sub>	-	-	200.0 g.
	Water to	-	-	1 litre.

## FORMULA VII.

25	Amidol	-	-	50 g.
	Sodium sulphite	-	-	100 g.
	Na <sub>2</sub> SO <sub>4</sub>	-	-	200 g.
	Water to	-	-	1 litre.

A suitable stop bath for terminating the action of these developer baths may have the following formula:

## FORMULA VIII.

	Sodium bisulphite	-	-	50 g.
	Glacial acetic acid	-	-	30 cc.
35	Water to	-	-	1 litre.

The following stop bath may be used with these developer baths as an alternative formula:

## FORMULA IX.

40	Glacial acetic acid	-	-	50 cc.
	Water	-	-	1 litre.

Each of these baths should be cooled to a temperature of 0°C. to 5°C. for use. Hydroquinone and its derivatives are very sensitive to temperature and are relatively inactive at low temperatures. For this reason the use of these stop baths at a low temperature brings about an immediate cessation of the developing action.

50 A 3% acetic acid solution may also be used as a stop bath for these developers.

The methods of control indicated above, additional to the presence of the loading agent, are as follows:—

55 1. The action of the processing bath is rapidly interrupted or terminated by means of a stop bath;

2. The layer is in a thoroughly dry con-

dition when the processing bath is applied;

3. The several layers of the film are separated by inert layers;

4. The temperature of the photographic element is suddenly and materially lowered. This step is more effective with certain baths than with others;

5. The layers may be somewhat hardened.

It is to be understood that these various means, while useful independently, are of greatest utility when used together, although all do not need to be used; some are more useful than others. The last mentioned two methods are of definitely minor importance.

Preferably the photographic material used is one in which two, three or more layers of differentially colour sensitized material are coated one upon another with intervening layers of inert material. Ordinarily gelatine is the material of all the layers, and all have the same permeability so that, unless otherwise controlled, the baths are able readily to diffuse through all the layers.

As examples of the loading agents which we may employ, various compounds may be mentioned. Among the organic liquids the higher alcohols have been found suitable. These include the primary, secondary, and tertiary forms such as normal propyl and isopropyl alcohols, the butyl alcohols and amyl alcohol. The ketones may be used, such as acetone and its homologues. Amines may be used, such as methyl, ethyl and propyl, and higher amines; tri-ethanol amine and other alkyl amines; acetylated alkyl amines such as (N-methyl)-acetamide, and acetamide. Among other substances

which may be used are ethylene and propylene glycol, dihydroxyethylene, or aqueous solutions of gelatine, glue or gums such as gum arabic dextrine, gum tragacanth, starches including flour and arrowroot and solutions of various solids such as sugar, and sodium chloride, potassium sulphate or other salts or mixtures thereof which are inert to the photographic process and whose solutions swell gelatine less than does plain water.

These compounds may be used alone or two or more may be used together as loading agents. We also include the use of substances which are soluble in mixtures of water and organic solvents. Various proportions may be used depending on the degree of retarding action desired. It has been found that a dye bleaching bath, for example, which penetrates a gelatine layer of .0005 inches thickness in one or two seconds can be so retarded that it will penetrate the same thickness of gelatine

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in four or five minutes by the addition of 75% of a loading agent to the solution. The time of penetration may be decreased or increased as desired by the addition of more or less loading agent.

5 Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to us by  
10 our foreign correspondents, we declare that what we claim is:—

1. A colour photographic process as claimed in the parent patent in which the loading agent is a water soluble substance  
15 capable of increasing the viscosity of the processing bath in which it is present.

2. A colour photographic process as claimed in the parent patent in which the loading agent is sugar.

20 3. A colour photographic process as claimed in the parent patent in which the loading agent is a water soluble cellulose derivative.

4. A colour photographic process as  
25 claimed in the parent patent in which the loading agent comprises one or more of the water-soluble higher alcohols.

5. A colour photographic process as claimed in the parent patent in which

the loading agent comprises one or more  
30 of the water-soluble ketones.

6. A colour photographic process as claimed in the parent patent, in which the loading agent comprises one or more  
35 of the water-soluble alkyl- or alkoxy- amines, acylated or not.

7. A colour photographic process as claimed in the parent patent, in which the loading agent comprises one or more  
40 of the polyhydric alcohols such as the glycols or glycerol.

8. A colour photographic process as claimed in the parent patent, in which the loading agent comprises one or more  
45 colloids such as gelatine, gum arabic or mixtures thereof.

9. A colour photographic process as claimed in the parent patent in which the loading agent comprises an inert salt,  
50 other than sodium sulphate, which can be employed in high concentration in the bleaching bath, such as potassium sulphate or sodium chloride.

Dated this 19th day of March, 1936.

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