

PATENT SPECIFICATION

Application Date: March 29, 1935. No. 9870/35.

454,499

(Patent of Addition to No. 427,520: Dated Sept. 21, 1932.)

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Complete Specification Accepted: Sept. 29, 1936.



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. 18936/34 (427,520) describes and claims a method of colour processing a photographic element having a plurality of superimposed layers containing different colour sensation silver salt records on the same side of a single support which includes colour developing all the silver salt records in the layers to one colour, fixing if necessary, and then bleaching the colour developed record in an upper layer in which such bleaching is effected by subjecting the element to the action of a bleaching agent which will remove and/or destroy the colour and will transform the silver which was developed therewith into a developable silver salt and which also contains a high concentration of a water soluble loading agent to retard the diffusion of said bleaching agent therethrough and such diffusion is arrested before the bleaching agent substantially penetrates into a lower layer and materially affects the image in such lower layer. Methanol is given as an example of a loading agent.

According to one feature of improvement in or modification of the invention claimed in application No. 18936/34 (427,520) water soluble substances capable of increasing the viscosity of the bleaching liquid are employed as loading agents, such as sugar or water soluble cellulose derivatives or water insoluble cellulose derivatives dissolved by the additions of organic solvents or mixtures thereof.

According to another feature of improvement in or modification of the invention claimed in application No.

18936/34 (427,520) 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. 18936/34 (427,520) 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. 18936/34 (427,520) 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. 18936/34 (427,520) 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. 18936/34 (427,520) 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 repellancy 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 agent.

FORMULA I.

A	{	Quinone	-	-	-	5 g.
		Methyl-alcohol	-	-	-	1000 cc.
		HCl	-	-	-	5 cc.
5 B	{	Sugar	-	-	-	300 g.
		Sodium chloride	-	-	-	50 g.
		Water	-	-	-	250 cc.

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

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. The photographic record element which is treated and which may be a film such as a motion picture film may have 2, 3 or more layers on the same side of the support.

In our co-pending application, No. 32441/34 (Nos. 440,032 and 447,092), we have disclosed a process 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.

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 decolourize 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 decolourize the dye and convert the silver to silver halide in this process may have one of the following formulæ in which iso-propyl 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.
Iso-propyl alcohol	-	-	-	1000 cc.
Glycerine	-	-	-	1000 cc.
Water	-	-	-	1000 cc.

In restricting the action of the bleaching agent it may be desirable to utilise one or more of the following additional methods of control.

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 condition 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 since certain of the steps are particularly useful in combination with certain other control means. 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 have the same diffusing properties as to all the layers.

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 ethyl alcohol, normal propyl, isopropyl, 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 nitrogen methyl acetamide, and acetamide. Among other substances which may be used are ethylene and propylene glycol, dihydroxyethyl-ether, 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.

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 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 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 the loading agent.

Dated this 27th 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 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, 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 parent specification No. 427,520 describes and claims a method of colour processing a photographic element having

a plurality of superimposed layers containing different colour sensation silver salt records on the same side of a single support which includes colour developing all the silver salt records in the layers to one colour, fixing if necessary, and then bleaching the colour developed record in an upper layer in which such bleaching is effected by subjecting the element to the action of a bleaching agent which will remove and/or destroy the colour and will transform the silver which was developed therewith into a developable silver salt and which also contains a high concentration of a water soluble loading agent to retard the diffusion of said bleaching agent therethrough and such diffusion is arrested before the bleaching agent substantially penetrates into a lower layer and

materially effects the image in such lower layer.

In the parent specification we have also claimed a method in which the loading agent is a water soluble organic liquid, specifically methanol. The present invention is concerned with the employment of various loading agents which have been found effective in carrying out the method claimed in the parent specification.

In our prior specification No. 427,518 we have claimed a colour photographic process of the type wherein the action of a bleaching bath or a developing bath has to be restricted to an upper layer of a plurality of layers on the same side of a single support in which control of diffusion of the bath is facilitated by the presence therein of a water soluble loading agent. In that prior specification we have also claimed such a process in which the loading agent is a water-soluble organic liquid, specifically methanol.

In the specification of patent 427,472 as open to inspection before the date of the present application there are disclosed a) a bleaching bath of the type with which the present invention is concerned, i.e. for colour developed images, in which methanol is employed as loading agent and b) a bleaching bath for silver images produced by ordinary development and a black and white developing bath in each of which sodium sulphate is employed as a loading agent; the present invention is not concerned with methods of bleaching silver images produced by ordinary development nor with developing baths.

According to one feature of improvement in or modification of the invention claimed in Specification No. 427,520 water soluble substances capable of increasing the viscosity of the bleaching liquid are employed as loading agents, such as sugar or water soluble cellulose derivatives or water insoluble cellulose derivatives dissolved by the additions of organic solvents or mixtures thereof.

According to another feature of improvement in or modification of the invention claimed in Specification No. 427,520 the loading agent comprises one or more of the water soluble higher 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. 427,520 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 Specification No. 427,520 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 Specification No. 427,520 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 Specification No. 427,520 the loading agent comprises one or more colloids such as gelatine or gum arabic or mixtures thereof.

According to another feature of improvement in or modification of the invention claimed in Specification No. 427,520 the loading agent comprises an inert salt, 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 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 repellancy between gelatine and the material added, materials producing this being alcohol and salts. The present invention however, does not include the employment of the 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 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 loaded bleaching baths suitable for use in the process claimed in the parent specification. The following formula illustrates a bleach bath which may be used to decolourize a dye in various types of multi-layer film, methyl alcohol, sugar and salt being used as the loading agent.

FORMULA I.

A	{	Quinone	-	-	-	5 g.
		(Methyl-alcohol	-	-	-	1000 cc.
		(HCl	-	-	-	5 cc.
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 silver image record in an upper layer of a multi-layer film as stated in

our co-pending application No. 9869/35 (Serial No. 454,498).

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. 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 applications 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 applied 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 metol-hydroquinone type of 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 decolourize 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 decolourize 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.	80
Iso-propyl alcohol	-	-	1000 cc.	
Water	-	-	75 cc.	
Quinone	-	-	5 g.	
HCl (concentrated)	-	-	20 cc.	

FORMULA III.

Glycerine	-	-	500 cc.	85
Iso-propyl alcohol	-	-	1000 cc.	
Quinone	-	-	5 g.	
HCl (concentrated)	-	-	50 cc.	

FORMULA IV.

Ethylene Glycol	-	-	500 cc.	90
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.	
Iso-propyl alcohol	-	-	1000 cc.	
Glycerine	-	-	1000 cc.	
Water	-	-	1000 cc.	105

In restricting the action of the bleaching agent it may be desirable to utilise one or more of the following additional methods of control.

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 condition 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 since 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 iso-propyl alcohols, the butyl alcohols and amyl alcohol. The ketones may be used, such as acetone and its homologues. Methyl, ethyl and propyl, and higher alkyl amines or alkoxy amines such as triethanol amine may be used, acylated or not. Examples of suitable acetylated alkyl amines are (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 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 of the loading agent. 60

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 our foreign correspondents, we declare that what we claim is:— 65

1. The improvement in or modification of the method claimed in the parent patent according to which a water soluble substance capable of increasing the viscosity of the bleaching solution is employed as loading agent. 70

2. The improvement in or modification of the method claimed in the parent patent according to Claim 1 in which a sugar is employed as loading agent. 75

3. The improvement in or modification of the method claimed in the parent patent according to Claim 1 in which a water soluble cellulose derivative is employed as loading agent. 80

4. The improvement in or modification of the method claimed in the parent patent according to which water soluble higher alcohols or mixtures thereof are employed as loading agents. 85

5. The improvement in or modification of the method claimed in the parent patent according to which water soluble ketones or mixtures thereof are employed as loading agents. 90

6. The improvement in or modification of the method claimed in the parent patent according to which water soluble alkyl- or alkoxy-amines, acylated or not, or mixtures thereof are employed as loading agents. 95

7. The improvement in or modification of the method claimed in the parent patent according to which polyhydric alcohols or mixtures thereof are employed as loading agents. 100

8. The improvement in or modification of the method claimed in the parent patent according to which water soluble colloids such as gelatine or gum arabic or mixture thereof are employed as loading agents. 105

9. The improvement in or modification of the parent patent in which inert salts, which can be employed in high concentration in the bleaching bath, are employed as loading agents. 110

Dated this 19th day of March, 1936.

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