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## AMENDED SPECIFICATION

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### PATENT SPECIFICATION

**454,622**

Application Date: March 29, 1935. No. 25940/36.

(Divided out of No. 454,498.)

(Patent of Addition to No. 427,518: dated Sept. 21, 1932.)

Complete Specification Left: March 20, 1936.

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:—

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

The Parent Specification No. 427,518 relates to the processing of photographic records 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 the 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 specification No. 427,518 the processing bath, the control of whose diffusion is facilitated by the presence therein of a water-soluble loading agent, is a colour developing bath, or a toning bath (including a dye-toning bath) or a fixing bath. According to another feature of improvement in or modification of the invention claimed in application 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 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 or 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.

In operating according to these further

features of improvement the bath, the control of whose diffusion is facilitated by the presence therein of the loading agent, may be a colour developing bath, or a toning bath (including a dye-toning bath) or a fixing bath.

The materials which are employed as loading agents may be of two general types which we believe to act as follows:

10 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

15 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

20 loading agents may act in both ways to produce an anti-swelling effect.

The following example illustrates the addition of loading agents to a colour developing bath. Such a developing bath

25 is the following:

A	{	2-amino-5-diethyl-amino-	
		toluene HCl - -	1 g.
		Sodium sulphite - -	10 g.
		Sodium carbonate -	30 g.
		Water to - -	1 litre.
B	{	<i>p</i> - nitro - phenyl - aceto-	
		nitrile - - -	0.75 g.
		Acetone - - -	20 cc.
		Iso-propyl alcohol -	100 cc.

Such colour developing baths containing loading agents may be used, for

30 example, as follows. A three layer film is immersed in a colour developer adapted to produce along with the silver image a dye image of the colour required in the top layer. The action of this

35 developer is restricted to the top layer by time control using some or all of the precautions hereinafter mentioned. After washing and drying the film is immersed in a colour developer adapted to produce

40 along with the silver image a dye image of the colour required in the middle layer. As before the action of the developer is restricted to the upper layer (which is inert to it) and the middle layer. The

45 film is again washed and dried and finally immersed in a colour developer appropriate to the lower layer.

Alternatively with a three-layer film we may develop all the layers to the colour

50 required in the bottom layer, then bleach the top two layers, then selectively colour redevelop the top layer, and finally colour develop the middle layer.

To enable the colour developing bath to

55 act sufficiently rapidly upon the layer to

which it is restricted it may contain a thiocyanate as described in our co-pending application No. 8920/35 (Serial No. 453,233).

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;

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 in 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 acetimide, and acetimide. 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 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 loading agent.

Dated this 23rd day of September, 1936.  
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. 427,518 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. In that specification we have claimed the employment of sodium sulphate 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 liquid such as methanol as a loading agent and have given an example for the use of methanol for this purpose in a chromic acid-bromide bleach bath for the colour developed layer. These examples 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 improvements in or modifications of the colour photographic process claimed in the parent patent.

According to one feature of improvement in or modification of the invention claimed in Specification No. 427,518 the processing bath, the control of whose diffusion is facilitated by the presence therein of a water-soluble loading agent, is a colour developing bath.

In carrying out the processing of photographic elements by the method of the parent patent (or as improved or modified in the manner defined above) it may be required to submit the element to a fixing bath or a toning bath (including a dye toning bath) whose action has to be restricted to an upper layer leaving a lower layer not materially affected thereby.

According to another feature of the invention, in a colour photographic process as claimed in the parent patent (or as improved or modified in the manner defined above) which also includes submitting the element to a fixing bath whose action has to be restricted to an upper layer leaving a lower layer not materially affected thereby, control of the diffusion of the fixing bath is facilitated by the presence therein of a water-soluble loading agent.

According to another feature of the invention, in a colour photographic process as claimed in the parent patent (or as improved or modified in the manner first defined above) which also includes submitting the element to a toning bath (including a dye toning bath) whose action has to be restricted to an upper layer leaving a lower layer not materially affected thereby, control of the diffusion of the toning bath is facilitated by the presence therein of a water-soluble loading agent.

The loading agents disclosed in the parent patent may be used.

Alternatively the loading agent may be sugar or sodium chloride or a mixture thereof or one or more of the water-soluble higher alcohols, i.e. containing more than two carbon atoms, or one or more of the water-soluble ketones or one or more of the water-soluble alkyl or alkoxy amines, acylated or not, or one or more of the polyhydric alcohols such as the glycols or glycerol, or one or more colloids such as gelatine or gum arabic or mixtures thereof, or an inert salt other than sodium sulphate which can be employed in high concentration in the bleaching bath, such as potassium sulphate or sodium chloride.

The employment of these alternative loading agents in the process claimed in Specifications Nos. 427,518 and 427,520 forms the subject of co-pending applications Nos. 9869/35 (Serial No. 454,498) and 9870/35 (Serial No. 454,499).

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.

An example of a colour developing bath to which loading agents may be added is the following:—

A	{	2 - amino - 5 - diethyl - amino - toluene - hydrochloride - - - 1 g.
		Sodium sulphite - - - 10 g.
		Sodium carbonate - - - 30 g.
		Water to - - - 1 litre.
B	{	<i>p</i> - nitro - phenyl - aceto-nitrile - - - 0.75 g.
		Acetone - - - 20 cc.
		Iso-propyl alcohol - 100 cc.

Such colour developing baths containing loading agents may be used, for example, as follows (see Specifications Nos. 440,032 and 447,092). A three layer film is immersed in a colour developer adapted to produce along with the silver image a dye image of the colour required in the type layer. The action of this developer is restricted to the top layer by time control using some or all of the precautions hereinafter mentioned. After washing and drying the film is immersed in a colour developer adapted to produce along with the silver image a dye image of the colour required in the middle layer. As before the action of the developer is restricted to the upper layer (which is inert to it) and the middle layer. The film is again washed and dried and finally immersed in a colour developer appropriate to the lower layer.

Alternatively with a three-layer film we may develop all the layers to the colour required in the bottom layer, then bleach the top two layers, then selectively colour redevelop the top layer, and finally colour develop the middle layer.

To enable the colour developing bath to act sufficiently rapidly upon the layer to which it is restricted it may contain a thiocyanate as described and claimed in our co-pending application No. 8920/35 (Serial No. 453,233).

In carrying out the selective colour development described above, it will be apparent that if a colour developed upper layer contains any developable salt, this must be removed by a fixing bath. The action of the fixing bath must be restricted to the upper layer by time control using some or all of the precautions hereinafter mentioned. To facilitate the necessary control of the penetration of the fixing bath it is, according to this invention, loaded with a large quantity of a water-soluble loading agent.

The necessity of differential fixation may also arise in cases where the image in an upper layer only is developed to silver and the image in a lower layer has then to be colour developed, as described for example in specification No. 440,032. Any developable silver salt which may remain along with the silver image in the upper layer must be removed before submitting the lower layer to the colour developer.

As described in specification No. 440,032, if a silver image exists in one layer only and the images in the other layers have been colour developed, the silver image may be colour by dye toning. If this silver image is in an upper layer the dye toning bath may, according to the present invention, contain a loading agent to assist in confining its action to the upper layer. Time control is employed to restrict the action of the toning bath to the upper layer using some or all of the precautions hereinafter mentioned.

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;
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; 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; triethanol-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 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. The time of penetration may be decreased or increased as desired by the addition of more or less loading agent.

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:—

1. The improvement in or modification of the colour photographic process claimed in the parent patent in which the developing bath, the control of whose diffusion is facilitated by the presence therein of a

water-soluble loading agent, is a colour developing bath.

2. A colour photographic process as claimed in the parent patent or in claim 1 hereof which also includes submitting the element to a fixing bath whose action has to be restricted to an upper layer leaving a lower layer not materially affected thereby, in which control of the diffusion of the fixing bath is facilitated by the presence therein of a water-soluble loading agent.

3. A colour photographic process as claimed in the parent patent or in claim 1 hereof and which also includes submitting the element to a toning bath (including a dye toning bath) whose action has to be restricted to an upper layer or layers leaving a lower layer not materially affected thereby, in which control of the diffusion of the toning bath is facilitated by the presence therein of a water-soluble loading agent.

4. A colour photographic process as claimed in any of claims 1 to 3 in which the loading agent is a water-soluble substance capable of increasing the viscosity of the processing bath in which it is present.

5. A colour photographic process as claimed in any of claims 1 to 3, in which the loading agent is sugar.

6. A colour photographic process as claimed in any of claims 1 to 3, in which the loading agent is a water-soluble cellulose derivative.

7. A colour photographic process as claimed in any of claims 1 to 3, in which the loading agent comprises one or more of the water-soluble higher alcohols.

8. A colour photographic process as claimed in any of claims 1 to 3, in which the loading agent comprises one or more of the water-soluble ketones.

9. A colour photographic process as claimed in any of claims 1 to 3, in which the loading agent comprises one or more of the water-soluble alkyl- or alkoxyamines, acylated or not.

10. A colour photographic process as claimed in any of claims 1 to 3, in which the loading agent comprises one or more of the polyhydric alcohols such as the glycols or glycerol.

11. A colour photographic process as claimed in any of claims 1 to 3, in which the loading agent comprises one or more colloids such as gelatine, gum arabic or mixtures thereof.

12. A colour photographic process as claimed in any of claims 1 to 3 in which the loading agent comprises an inert salt which can be employed in high concentration in the bleaching bath, such as potassium sulphate, sodium sulphate or sodium chloride.

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Dated this 23rd day of September, 1936.

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