PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in and relating to Colour Photographic Films Bearing Sound Tracks and Methods for Producing the same

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, 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 Company organised under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York, United States of America, to be as follows:—

This invention relates to colour photographic films bearing sound tracks, and methods for producing sound tracks on such films.

In many cases, where motion picture films are produced carrying coloured visual images, it is difficult or impossible to provide a silver sound track along with the coloured or dyed picture areas. The principal object of the present invention is to provide a sound track of suitable characteristics on such a film. The invention is particularly applicable to motion picture films having colour images in a plurality of layers inseparably coated upon a single support, i.e. of the monopack type, for example films in which all the layers are on the same side of the support. In most cases, the dye or other colour images in monopack films are unsatisfactory for recording on a photo-electric cell; moreover, the scattering of the light on its passage through one or more emulsion layers impairs the resolving power and accordingly impairs the recording of high frequencies.

According to the present invention, a multi-layer colour photographic film carries a sound track image wholly or principally in the upper emulsion layer or in the layer which is first hit by the incident light and composed of silver sulphide. The use of silver sulphide for the production of a sound track image was proposed in Specification No. 382,506, but this specification was concerned only with the production of a sound-picture film where the picture images were formed by dye imbibition. Moreover, it has been suggested to form the sound track image in the red sensitive layer of a monopack film in which such red sensitive layer was either the bottom or the top layer. A sound track image present wholly or mainly in the top layer and formed of silver sulphide presents advantages in sound recording and sound reproduction not hitherto realised.

An important feature of the invention consists in processing a sound track image in the upper layer only of a multilayer photographic film to silver sulphide and processing the visual images to pure dye images by operations involving colour development.

In the film described by way of example in our copending applications Nos. 17743/34 (Serial No. 440,032) and 16012/35 (Serial No. 447,092), the minus-red image which is the only one of the three dye images at all suitable for the sound track, owing to its red absorption, (i.e., density with respect to the caesium cell sensitivity), is in the bottom or inner emulsion layer. If the image is recorded from the emulsion side of the film, the passage of the light through the upper two emulsions lowers the resolving power of the image produced in the lower layer considerably below the required limit. To record the image through the support would require local or total removal of the anti-halation backing with the inevitable danger of halation, and in any case there would be the risk of producing noise during reproduction owing to the recording in the lower layer of any scratches there might be on the support. On the other hand, the blue sensitive layer, which is the outer emulsion layer in the preferred form described in the aforementioned applications, is particularly well suited to the requirements of a sound track, and its already high resolving power (for blue light) is further increased by the yellow filter dye which may be distributed therethrough. The yellow (minus blue) dye image which is produced in this layer is practically useless for sound reproduction, since it is almost transparent to the light to which the photo-electric cell is sensitive. It is quite possible, however, to utilise the silver which exists along with

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the dye in this top layer by converting it into silver sulphide instead of removing it.

The invention, of course, is not limited to the films described above by way of example, since it may be utilised for any films of the monopack type, e.g., the film described in our copending application 16013/35, where the sensitive emulsions are distributed on opposite sides of the support. Moreover, the invention is not limited to film in which the visual images consist of dyes produced by colour development, since it may be applied to films in which the coloured visual images are produced by mordanting, dye-toning or imbibition.

In all cases, the sound record in the upper layer is converted into silver sulphide at such appropriate stage of the processing that the silver sulphide will remain unaffected by any later steps in the processing (for example in colour developing the layers), if such are required. The silver sulphide image may afterwards be intensified, for example, by physical development with silver, but in general this is not necessary or even desirable, since a sulphide image of suitable density may readily be obtained directly from the original silver image in the upper emulsion layer.

Where the film is to be processed to a negative, the sound track record may be confined to the top layer by exposure of the sound track through a filter which cuts out all light to which the other layers are sensitive, i.e., a blue filter in the case where the blue sensitive layer is uppermost, and the under layers are protected by a yellow filter. If the film is to be processed to a positive by reversal, the sound track may be restricted to the upper layer only, by one of two methods. The first is to record the sound through a filter of the same character as that indicated for negative processing, and then fully to expose the under-layers to light to which they are sensitive, but to which the upper layer is insensitive, e.g., yellow light in the case where the upper layer is blue sensitive and the under-layers are respectively red and green sensitized. Upon reversal, the under layers are entirely clear, and the image is left in the upper layer only.

The second method, which is particularly applicable when the film is exposed directly in the camera, is to use a light for sound recording, which will produce an image of correct density in the upper layer, but will over-expose the lower layers. In the case where the blue sensitive layer is uppermost, a light containing a predominant proportion of orange-yellow may be employed, i.e., from a low temperature lamp.

It will be apparent that by proceeding in any of these ways, the record in the sound track is principally in the upper emulsion layer, the under-layers being relatively or entirely clear of any image or residue.

The conversion of the sound track image to silver sulphide may be effected at any stage in the processing when there is still silver in the image, preferably at some stage when the film is dry. In the method of processing described in detail in copending applications 17743/34 and 16012/35, the most suitable point at which to effect this conversion is immediately after development of all the layers to minus red and after fixation, if this is employed, since at this point the film is dried. The image in the sound track may be selectively bleached to silver halide or other suitable silver salt, such as silver ferro-cyanide by localized application of a bleaching agent, to the sound track portion of the film e.g., by an applicator-roller or other known device. Subsequent washing and immersion of the film in a solution of a soluble sulphide will cause the conversion of the bleached image which exists in the sound track only to silver sulphide, and this silver sulphide image will remain unaffected by the subsequent steps in the differential processing of the layers. It does not matter whether the minus red dye image remains associated with the silver sulphide in the sound track, since it will be removed by the subsequent bleach baths employed in the differential treatment of the visual records. Suitable bleaching baths for bleaching the sound track image are:

(1) An alkali metal ferri-cyanide, used alone or with alkali and with or without a soluble halide.

(2) A bleach bath of the copper chloride or copper bromide type, such as is well known for the bromoil process and for processes requiring selective gelatine hardening.

(3) Iodine and potassium iodide solution.

(4) A chromic acid bleach bath.

The soluble sulphide employed may be sodium, potassium or ammonium sulphide.

As an alternative to the use of a solution of a soluble sulphide, the sound track may be exposed to hydrogen sulphide gas, provided that the film is wet and that sufficient alkali is present to neutralize the acid released. The method of producing a silver sulphide image by exposure to gases is described in the Photographic Journal, March, 1923, at Page 110. The preferred method of producing a silver

sulphide image in the upper layer only of the sound track when carrying out the present invention, is locally to moisten the sound track with water applied, for example, by means of a flanged applicator roller, the flange of which bears against the edge of the film. The subsequent processing of the moistened sound track portion of the film can then be accomplished by means of gaseous reagents which have no effect upon the remaining dry part of the film carrying the visual images. Since the applicator roller has to apply only water, there is available a wider selection of materials for its construction. When only the sound track portion of the film has been moistened the film is passed into a vessel containing halogen vapour, for example, bromine, which converts the silver in the moistened portion only of the film to silver bromide, which is accomplished in a few seconds. After a few seconds' exposure to air the film is passed into a vessel containing a mixture of ammonia and hydrogen sulphide vapour, to which it is exposed for a few seconds. This converts the silver bromide only in the moistened portion to silver sulphide. After drying, the film may be submitted to further processing without any preliminary washing.

Alternatively, a flanged applicator roller or other suitable device may be employed to apply a solution of a soluble sulphide to the sound track portion of the film after it has been subjected to a bleaching bath which reconverts the silver in the upper layer or upper layers to to silver salt.

The result of the present invention is to produce a film in which, however the visual images have been selectively colour processed, the sound image in the sound track exists wholly or mainly in the upper layer in the form of silver sulphide. For example, in the case of a three-layer film, the visual images may be processed by methods of colour development producing clear transparent dye images in the layers while the sound image in the upper layer of the sound track consists of silver sulphide.

The invention may obviously be applied to films having sound track of the variable width or variable density type.

Dated this 19th day of December, 1935.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1.
Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in and relating to Colour Photographic Films Bearing Sound Tracks and Methods for Producing the same

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, 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 Company organised under the Laws of the State of New Jersey, 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 multi-layer colour photographic films bearing sound tracks, and methods for producing sound tracks on such films.

It is known that the use of an opaque silver or silver salt image for the sound record possesses advantages over the use of a dye image.

In many cases, where motion picture films are produced carrying coloured visual images, it is difficult or impossible to provide a silver sound track along with the coloured or dyed picture areas. This is particularly the case when some or all of the colour images are produced by colour development since an important step in a process involving colour development is the removal of the silver from the dye images. In the processing of multi-layer films by methods involving colour development, moreover, the film is subject to reagents of very different composition from those usually employed in other processes, e.g. dye imbibition processes; in one or more stages the film is generally subjected to a reagent which bleaches the silver image and/or the dye image. Bleaching baths which convert silver into a silver halide or other salt are often employed.

According to the present invention, a multi-layer colour photographic film in which some or all of the visual images have been produced by colour development carries a sound track image composed of silver sulphide and wholly or principally in the upper emulsion layer which was upon exposure first hit by the incident light. Silver sulphide is not only very insoluble but possesses other advantages rendering it particularly suitable for use in a multi-layer photographic film of the kind indicated. It is not attacked by the

bleaching baths used in processing multilayer films by methods involving colour development, such as are employed, for example, in the processes of our applications Nos. 440,032, 440,089 and 447,092. Moreover it gives an opaque image almost non-selective as to colour and as to different photo-electric cells. It is also capable of being intensified if desired. The use of silver sulphide for the production of a sound track image in an imbibition process was proposed in our Specification No. 382,506. It has been suggested to form the sound track image in the red sensitive layer of a monopack film in which such red sensitive layer was either the bottom or the top layer and it has also been proposed to form the sound record in silver in the blue sensitive layer of a three-layer film having dyestuffs or dyestuff-forming substances diffusedly incorporated therein, such blue layer being either below or above or between the other layers.

According to the method of the present invention a sound track image in the upper layer of a multi-layer photographic film is processed to silver sulphide and the visual images are processed to pure dye images by operations involving colour development.

In the film described by way of example in our applications Nos. 440,032 and 447,092, the minus-red image which is the only one of the three dye images at all suitable for the sound track (since it is the only image which absorbs red light sufficiently to enable it to be used in conjunction with a caesium cell which, as is known, is sensitive to red light), is in the bottom or inner emulsion layer. If the image is recorded from the emulsion side of the film, the passage of the light through the upper two emulsions lowers the resolving power of the image produced in the lower layer considerably below the required limit. To record the image through the support would require local or total removal of the anti-halation backing with the inevitable danger of halation, and in any case there would be the risk of producing noise during reproduction owing to the recording in the lower layer of any scratches there might be on the support. On the other hand, the blue sensitive layer, which is the outer emulsion layer in the preferred form described in the aforementioned applications, is particularly well suited to the requirements of a sound track, and its already high resolving power (for blue light) is further increased by the yellow filter dye which may be distributed therethrough. The yellow (minus blue) dye image which is produced in this layer is practically useless for sound reproduction, since it is almost transparent to the light to which the photo-electric cell is sensitive. It is quite possible, however, to utilise the silver which exists along with the dye in this top layer by converting it into silver sulphide instead of removing it.

The invention, of course, is not limited to the films described above by way of example, since it may be utilised for any films of the monopack type, e.g., the film described in our application No. 440,089, where the sensitive emulsions are distributed on opposite sides of the support.

In all cases, the sound record in the upper layer is converted into silver sulphide at such appropriate stage of the processing that the silver sulphide will remain unaffected by any later steps in the processing (for example in colour developing the layers), if such are required. The silver sulphide image may afterwards be intensified, for example, by physical development with silver, when it is of sufficient density but in general this is not necessary or even desirable, since a sulphide image of suitable density can usually be obtained directly from the original silver image in the upper emulsion layer, such intensification of a silver sulphide image is described in British Journal of Photography, 1934 p.p. 212—214.

Where the film is to be processed to a negative, the sound track record may be confined to the top layer by exposure of the sound track through a filter which cuts out all light to which the other layers are sensitive, i.e., a blue filter in the case where the blue sensitive layer is uppermost, and the under layers are protected by a yellow filter. If the film is to be processed to a positive by reversal, the sound track may be restricted to the upper layer only, by one of two methods. The first is to record the sound through a filter of the same character as that indicated for negative processing, and then fully to expose the under-layers to light to which they are sensitive, but to which the upper layer is insensitive, e.g., yellow light in the case where the upper layer is blue sensitive and the under-layers are respectively red and green sensitized. Upon reversal, the under layers are entirely clear, and the image is left in the upper layer only.

The second method, which is particularly applicable when the film is exposed directly in the camera, is to use a light for sound recording, which will produce an image of correct density in the upper layer, but will over-expose the lower layers. In the case where the blue sensitive layer is uppermost, a light contain-

ing a predominant proportion of orange-yellow may be employed, i.e., from a low temperature lamp.

It will be apparent that by proceeding in any of these ways, the record in the sound track is principally in the upper emulsion layer, the under-layers being relatively or entirely clear of any image or residue.

The conversion of the sound track image to silver sulphide may be effected at any stage in the processing when there is still silver in the image, preferably at some stage when the film is dry. In the method of processing described in detail in our applications Nos. 440,032 and 447,092, the most suitable point at which to effect this conversion is immediately after development of all the layers to minus red and after fixation, if this is employed, since at this point the film is dry. The image in the sound track may be selectively bleached to silver halide or other suitable silver salt, such as silver ferro-cyanide by localized application of a bleaching agent to the sound track portion of the film, e.g., by an applicator-roller or other known device. Subsequent washing and immersion of the film in a solution of a soluble sulphide will cause the conversion of the bleached image which exists in the sound track only to silver sulphide, and this silver sulphide image will remain unaffected by the subsequent steps in the differential processing of the layers. It does not matter whether the minus red dye image remains associated with the silver sulphide in the sound track, since it will be removed by the subsequent bleach baths employed in the differential treatment of the visual records. Suitable bleaching baths for bleaching the sound track image are:—

(1) An alkali metal ferri-cyanide, used alone or with alkali and with or without a soluble halide.

(2) A bleach bath of the copper chloride or copper bromide type, such as is well known for the bromoil process and for processes requiring selective gelatine hardening.

(3) Iodine and potassium iodide solution.

(4). A chromic acid bleach bath.

The soluble sulphide employed may be sodium, potassium or ammonium sulphide.

As an alternative to the use of a solution of a soluble sulphide, the sound track may be exposed to hydrogen sulphide gas, provided that the film is wet and that sufficient alkali is present to neutralize the acid released. The method of producing a silver sulphide image by exposure to gases is described in the Photographic Journal, March, 1923, at Page 110. The preferred method of producing a silver sulphide image in the upper layer only of the sound track when carrying out the present invention, is locally to moisten the sound track with water applied, for example, by means of a flanged applicator roller, the flange of which bears against the edge of the film. The subsequent processing of the moistened sound track portion of the film can then be accomplished by means of gaseous reagents which have no effect upon the remaining dry part of the film carrying the visual images. Since the applicator roller has to apply only water, there is available a wider selection of materials for its construction. When only the sound track portion of the film has been moistened the film is passed into a vessel containing halogen vapour, for example, bromine, which converts the silver in the moistened portion only of the film to silver bromide, which is accomplished in a few seconds. After a few seconds' exposure to air the film is passed into a vessel containing a mixture of ammonia and hydrogen sulphide vapour, to which it is exposed for a few seconds. This converts the silver bromide only in the moistened portion to silver sulphide. After drying, the film may be submitted to further processing without any preliminary washing.

Alternatively, a flanged applicator roller or other suitable device may be employed to apply a solution of a soluble sulphide to the sound track portion of the film after it has been subjected to a bleaching bath which reconverts the silver in the upper layer or upper layers to silver salt.

By way of example, a film having three layers inseparably coated on the same side of a single support of which the upper layer contains the blue colour record, the middle layer the green colour record, and the bottom layer the red colour record, may after exposure, and if necessary reversal of the images, be processed to produce images of metallic silver and blue green dye in the picture area and the sound track area. In order to convert the images in the sound track area into silver sulphide images, mainly existing in the upper layer, water may be applied to the sound track area only, by means of an applicator roller. The water may contain a small amount of a suitable wetting agent such as saponin, to overcome the surface repellency of the emulsion and a small amount of a moisture retaining agent such as glycol or glycerine, in order to prevent drying out of the moistened strips at the edges during the subsequent gas-treating process.

After being moistened on the sound

track portion, the film is passed through a slit into a long vertical chamber provided with rollers at its lower and upper ends around which the film may be continuously drawn. In this chamber, it is treated with chlorine which may be supplied at the bottom. The film then passes out of this chamber in which it is washed free of bleaching gas by a current of air after which it enters another chamber, similar to the first. The humidity of the current of air passed through the chamber must be carefully controlled to prevent drying of the moistened film. The current of air is for the purpose only of removing the chlorine or bromine bleaching gas, and is preferably passed upwards through the chamber.

When the film passes into the third chamber, it is treated with the vapour of ammonium sulphide or hydrogen sulphide, which is also supplied at the bottom. After this treatment, the film passes out of the apparatus through an exit slit through a washing chamber, where it is washed with a spray of liquid such as water, then if desired squeegeed, and finally passed through a drying chamber.

Preferably, the gas treatment chambers are provided with suction devices at their upper ends. Since both of the gases used are heavier than air, they are retained in the vapours by gravity, but any air leaking in is immediately drawn away, although the reaction gases are only lost to a small extent.

It is important to control the humidity during the entire gas toning operation. If the humidity is too low the moistened strip may become edge-dried and if the humidity is too high, the picture area may be visibly affected and objectionable surface deposits may be formed. The gas toning operation should preferably be carried out at a temperature of 60° F. or lower. The humidity should be between about 40% and about 60%. This humidity must also be maintained sufficiently high in the drying chamber 13 to prevent drying during the removal of the halogen gas. This chamber is kept at a temperature of 50 to 60° F., and a relative humidity of between 40% and 60%.

It is also important to remove any traces of free sulphide from the toned film before the subsequent bleaching and colour-forming development steps of our process. The purpose of the bleaching step following the recording of the sound according to our preferred method is to transform the silver images in certain layers of the picture area to silver halide which is developable. The presence of any free sulphide in the bleach bath causes the silver image being bleached to be transformed to opaque silver instead of to silver halide. Such contamination of the picture with silver sulphide would mean sacrificing picture quality in order to obtain good sound quality.

The free sulphide is removed from the film by washing the film by a spray of water. The water jets are preferably directed obliquely across the film from the picture area toward the sound track. This washing is followed by squeegeeing the film after which it passes through a drying chamber, in which it is thoroughly dried, preferably by the use of warm air. The film may also be treated with chlorine or bromine gas or with a solution of chlorine or bromine, to oxidize any unused sulphide on the film.

A second method for sulphiding the sound track employs the application of a liquid bath containing a soluble sulphide. The bath employs a quinone bleaching agent and hydrochloric acid and converts the sound track to silver sulphide in a single operation. The liquid sulphiding bath may be applied by applicator 11 in the same manner as the water of the gas toning method. A suitable liquid sulphide bath may have the following composition:

Glycerine	100 grams
Hydrochloric acid	20 grams
Quinone	5 grams
Sodium sulphide	35 grams
Water	1 litre

The sodium sulphide used in this formula may vary from a few tenths of 1% to about 3% or more of the amount of solution by weight.

In this method of sulphiding an after-treatment is also necessary to oxidize or remove unused sulphide. This may be done by treating with chlorine or bromine gas as described above, or by strip application of a chlorine or bromine solution.

After the sulphiding described above has been completed and the film has been washed and dried, it is then ready for the remaining processing steps to form coloured images in the picture area.

The result of the present invention is to produce a film in which, however the visual images have been selectively colour processed, the sound image in the sound track exists wholly or mainly in the upper layer in the form of silver sulphide. For example, in the case of a three-layer film, the visual images may be processed by methods of colour development producing clear transparent dye images in the layers while the sound image in the upper layer of the sound track consists of silver sulphide.

The invention may obviously be applied to films having sound tracks of the variable width or variable density type.

Having now particularly described and ascertained the nature of our 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. A multi-layer colour photographic sound and picture film in which some or all of the visual images have been produced by colour development having a sound track image composed of silver sulphide, and wholly or principally in the upper emulsion layer which was upon exposure first hit by incident light.

2. A multi-layer colour photographic sound and picture film as claimed in claim 1, in which the upper emulsion layer first hit by incident light carries in the picture area a record of the blue colour component.

3. A multi-layer colour photographic sound and picture film as claimed in claim 1, having three emulsion layers on a single support respectively containing records in the picture area of the red, green and blue colour components of which that layer containing the blue colour component record is an outer layer and contains in the sound area a sound image in silver sulphide.

4. A multi-layer colour photographic sound and picture film as claimed in claim 1, having three emulsion layers inseparably coated on the same side of a single support respectively containing records in the picture area of the red, green and blue colour components of which that layer containing the blue colour component is furthest from the support and contains in the sound area a sound image in silver sulphide.

5. The method of producing a multilayer colour photographic sound and picture film in which a sound track image in the upper layer of a multilayer photographic film is processed to silver sulphide and the visual images are processed to pure dye images by operation involving colour development.

6. The method as claimed in claim 5 which consists in forming images of metallic silver and dye in both sound and picture areas, converting the silver sound image existing in the upper layer to silver sulphide and processing the images in the picture area to dye images by operations involving colour development without affecting the sound image.

7. The method as claimed in claim 5 which consists in forming images of metallic silver in both sound and picture areas, converting the sound image existing in the upper layer to silver sulphide without affecting the picture images, treating the film with a reagent which affects metallic silver but not silver sulphide to convert some or all of the colour images in the picture area to developable silver salt and colour developing the images in the picture area.

8. The method as claimed in claim 5, 6 or 7 in which the film is one in which all the emulsion layers are inseparably coated on the same side of a single support.

9. The method as claimed in claims 5—8 in which the image in the sound area is confined principally to the upper layer by exposure to a light to which the other layers are not sensitive or from which they are protected.

10. The method as claimed in claims 5—8 in which the film is treated for the production of reversed images in all the layers and the image in the sound area is confined principally to the upper layer by fully exposing the under-layers of the sound area before reversal.

11. The method as claimed in claims 5—8 in which the film is treated for the production of reversed images in all the layers and the image in the sound area is confined principally to the upper layer by recording it with a light of suitable colour to give correct exposure of the outer layer and over exposure of the under-layers.

12. The method as claimed in any of claims 5 to 11 in which the silver image in the sound area is converted to silver sulphide by localised application of a bleaching agent followed by localised application of a sulphiding agent.

13. Multi-layer colour photographic sound and picture films produced by colour development and methods for their production, substantially as herein described.

Dated this 23rd day of December, 1936.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

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