

SPECIFICATION

Treatment of an exposed photographic film to increase the effective speed thereof

5 The present invention relates to photographic film processing, being concerned with processes for increasing the effective "speed" of such films (defined in terms of the minimum energy required to
10 record a detectable image).

The primary ways in which photographic films have heretofore been rendered more sensitive or of increased speed, are as follows. First, the size of the silver halide crystals in the light sensitive emulsion
15 has been increased to increase the probability of photon absorption. Secondly, the crystals may be chemically sensitized during preparation to increase the efficiency of electron-trapping, as electrons are released upon photon impact. Thirdly, in the proces-
20 sing, more efficient reducing agents have been employed to discriminate between exposed and non-exposed crystals.

One of the common methods of rating the photographic speed of film is in terms of the minimum
25 camera exposure required to produce a recorded threshold image. This is expressed in terms of relative ASA speed ratings, the values of which increase in correspondence with increases in the speeds of films. Present-day techniques permit ASA
30 ratings of the order of 2000 for very high-speed black and white negative films, and of the order of 400-500 for high-speed reversal colour films. In order to increase the effective speed of the negative type film, prolonged development may be employed to
35 increase the slope of the density versus log of exposure characteristic curve (D-Log E) near the toe of the curve, but with a sacrifice of quality in the reduction of the available exposure range or latitude and fogging. Factors of two to three in effective
40 speed increase can, however thus be obtained. Forced development of reversal colour films will also produce an apparent increase in speed, for strong images, but actually no increase in the image-
45 recording threshold at the toe of the D-Log E curve or the shoulder of its reversal curve.

Underlying the present invention, however, is the startling discovery of a process with which black and white negative, colour reversal and negative films and other photographic media can be processed to
50 increase their effective speeds to degrees previously unattainable, and with minimal sacrifice of quality and exposure latitude, and with very substantial boosting or amplification of threshold image-
55 recording in the toe of the D-Log E characteristic. This has opened up new opportunities in photo-instrumentation, particularly in underwater applications, as in peat-stained lakes, where light attenuation may be severe and the range of photography
60 most limited.

An object of the invention, accordingly, is to provide a process for increasing the effective speed of photographic films and other photographic media that is not subject to the above-described limitations of prior techniques.

65 In accordance with the present invention, there is

provided a process of treating an exposed black-and-white or colour photographic medium (hereinafter referred to as 'film') to increase the effective speed thereof, comprising: developing and fixing the
70 black-and-white reduced silver image, said image being not discernible by the eye, converting the reduced silver of the image to a silver complex, and re-developing the film in a colour coupling developer in the presence of colour coupler to provide an
75 enhanced colour image.

According to one aspect of the invention, there is provided a process of treating an exposed black-and-white photographic medium (hereinafter referred to as 'film') to increase the effective speed thereof,
80 comprising: developing and fixing the black-and-white reduced silver image, said image being not discernible by the eye, converting the reduced silver of the image to a silver complex, and re-developing the film in a colour coupling developer in the
85 presence of colour coupler to provide a colour image enhanced relative to the silver image.

According to another aspect of the invention, there is provided a process of treating an exposed colour photographic medium (hereinafter referred to as
90 'film') having colour coupler in the film layers and renderable as a colour negative to increase the effective speed thereof, comprising developing and fixing the black-and-white reduced silver image, said image being not discernible by the eye, converting
95 the reduced silver of the image to a silver complex, and re-developing the film in a colour coupling developer in the presence of colour coupler to provide an enhanced colour image.

The invention is illustrated by the following examples.
100

Example 1

Turning, first to the application of the invention to black and white negative film, it will be recalled that
105 the D-Log E characteristic curve shows a long, just slightly rising, almost horizontal toe emerging into a constant steep slope region which then shoulders off in saturation. The threshold of image recording lies within the almost horizontal toe. While, as before
110 stated, prior techniques of forced development will somewhat tilt the toe upward to provide a lower effective image-recording threshold, this is limited by the inherent development of all silver-halide crystals (whether exposed or not) and the conse-
115 quent fogging with resultant loss in effective overall film speed.

In accordance with this example, the black and white negative film (such as Eastman Recording Film 2475) is first force-developed in conventional black
120 and white developer (such as phenyl methyl pyrazolidone) to produce maximum speed with minimum fog. It has been found to be preferred for the purposes of the invention that the temperature be maintained cool, around 75°C, and the time of the
125 developing of the order of 12 minutes. The film is then fixed by dissolving out the undeveloped silver halide crystals, as with sodium thiosulphate, leaving only the final reduced silver image. Following washing, the reduced silver image is completely
130 converted to a soluble silver complex by re-

halogenation with a bleaching agent, such as potassium ferricyanide.

After washing, the film is re-developed, but this time in a colour-coupling developer such as 4-amino-N-ethyl-N-(B-methanesulphonamidoethyl)-m-toluidine sesquisulphate monohydrate (sold, for example, by Eastman Kodak under type 'Colour Developing Agent CD-3'), to which has been added a colour coupler such as 2,4-dichloro-1-naphthol (cyan or blue-green), or any similar desired colour dye. This re-developing stage is allowed to proceed to completion (of the order of about eight minutes at room temperature), reducing the image to silver and, in this case, blue-green colour dye proximal to the silver. The colour-coupling developer is removed by washing, and the silver is again completely converted to a soluble silver complex with the above-mentioned re-halogenation bleaching agent, following which the film is fixed, as before described, this time to remove all traces of silver. The film is then washed and dried.

It has been found that this process enables undetectable images in the film after the first development step, now to be clearly indicated, this time in the colour of the colour coupler. Otherwise stated, the threshold of detectable image-recording has been markedly lowered, with the image manifesting itself by the colour dye. What appears to have happened is that, if the right proportions are used, each exposed silver unit can be replaced by a number of colour dye units; multiple dye units being more visible than a single silver unit that they replace. In the above example, 6 units of colour coupler were used for every 2 units of the CD-3 colour coupling developer, producing an image speed increase of a factor of four. Such proportions represent, of course, radical departures from those used for other objectives in usual colour film development (such as 3 units of CD-3 for 1 units of colour coupler, as in Kodak's "Kodachrome" developing procedures).

Returning to the D-Log E curve, the almost horizontal toe, representing few exposed silver units, has been effectively turned upward with a greater slope corresponding to this amplification or effective enhancement, and thus providing an effective increase in photographic film speed, without the relatively rapid fogging density effect in ordinary prior prolonged development processes, before mentioned.

By this technique, the exemplary 2475 film ASA rating of about 2000 has been startlingly boosted to about 8000 and above, even up to ASA ratings of the order of 20,000.

Example 2

The steps of Example 1 were repeated, but increased contrast for the faintest images were obtained by then re-cycling or repeating the soluble silver complex-colour coupling, re-developing and subsequent steps. The contrast was found to be approximately doubled with the re-cycling procedure.

Example 3

In this example, colour film (Kodak "Ektachrome" VNX, ASA 400) was successfully rendered as a colour negative and provided with greatly increased speed by the process of the invention.

The exposed colour film was first developed in a black-and-white phenyl methyl pyrazolidone developer (about 5 minutes at 70°C) and then fixed to produce a black and white negative. After washing, the reduced silver image was converted completely to a soluble silver complex as in Example 1.

Following washing, the film was re-developed, this time in the colour-coupling developer of Example 1, but without the addition of the colour coupler in view of the presence of colour-coupling dye units already incorporated in each layer of the film.

The silver was again converted to the soluble silver complex by the re-halogenating bleaching agent of Example 1, and the film was fixed, washed and dried, resulting in a full true colour negative image with vastly increased speed.

By re-cycling the soluble silver complex/re-developing and bleaching or re-halogenating and fixing steps, an ASA of 20,000 was attained.

Photographs taken by strobe lighting of objects at distances of the order of thirty feet in the heavily peat-stained waters of Loch Ness, Scotland, and completely undetectable in the black and white negative stage, became for the first time readily apparent in the colour negative thus processed.

There are instances, moreover, such as where colour discrimination is not important, wherein the silver units may be kept in the developed product together with the proximal colour units achieved by the colour-coupling developer re-developing step. An example of such follows as:

Example 4

The steps of Example 1 were repeated up to and including the re-development in the colour-coupling developer CD-3 with the added cyan colour coupler. The colour-coupling developer was then removed by washing and the film was then dried.

This could be re-halogenated with a re-cycling of the colour-coupling developing step to attain even greater gain as contrast.

While the invention has been described in connection with particular exemplary films, it is to be understood that the process is equally useful with other films of similar or related characteristics. The application is divided from Application No. 2034060A.

CLAIMS

1. A process of treating an exposed black-and-white or colour photographic medium (hereinafter referred to as "film") to increase the effective speed thereof, comprising: developing and fixing the black-and-white reduced silver image, said image being not discernible by the eye, converting the reduced silver of the image to a silver complex and re-developing the film in a colour coupling developer in the presence of colour coupler to provide an



halogenation with a bleaching agent, such as potassium ferricyanide.

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enhanced colour image.

2. A process of treating an exposed black-and-white photographic medium (hereinafter referred to as "film") to increase the effective speed thereof,

- 5 comprising: developing and fixing the black-and-white reduced silver image, said image being not discernible by the eye, converting the reduced silver of the image to a silver complex, and re-developing the film in a colour coupling developer in the
10 presence of colour coupler to provide a colour image enhanced relative to the silver image.

3. A process of treating an exposed colour photographic medium (hereinafter referred to as "film") having colour coupler in the film layers and

- 15 renderable as a colour negative to increase the effective speed thereof, comprising developing and fixing the black-and-white reduced silver image, said image being not discernible by the eye, converting the reduced silver of the image to a silver complex,
20 and re-developing the film in a colour coupling developer in the presence of colour coupler to provide an enhanced colour image.

4. A process according to any preceding claim, wherein the step of converting the reduced silver of
25 the image to a silver complex is effected by bleaching.

5. A process according to claim 4, wherein the converting is effected with potassium ferri-cyanide as bleaching agent.

- 30 6. A process according to any preceding claim, wherein the converting and re-developing steps are repeated at least once.

7. A process according to any preceding claim, further comprising, after the re-developing of the
35 film, removing silver produced during the re-developing.

8. A process according to claim 7, wherein the silver is removed by converting it to a soluble silver complex and then fixing the film.

- 40 9. A process according to claim 8, wherein the converting step in the removal of the silver is effected by bleaching.

10. A process according to claim 9, wherein the bleaching in the removal of the silver is effected with
45 potassium ferri-cyanide as bleaching agent.

11. A process according to any of claims 7 to 10, wherein, after the removal of the silver, the film is washed and dried.

12. A process according to any preceding claim,
50 wherein the first-mentioned developing is effected with phenyl methyl pyrazolidone as developer.

13. A process according to any preceding claim, wherein the fixing is effected with sodium thiosulphate as fixer.

14. A process according to any preceding claim, wherein the re-developing is effected with 4-amino-N-ethyl-N-B methanesulphonamidoethyl)-m-toluidine sesquisulphate monohydrate as developer.

15. A process according to any preceding claim,
60 wherein the step of converting the reduced silver of the image to a silver complex is carried out in the absence of added halogen.

16. A process according to claim 1, substantially as described herein in any of Examples 1 to 4.