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### PATENT SPECIFICATION

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### PROVISIONAL SPECIFICATION

#### Improvements in or relating to Colour Photography

I, DOUGLAS ARTHUR SPENCER, a British Subject, of 118, Fulham Road, South Kensington, London, S.W.3, do hereby declare the nature of this invention to be as follows:—

This invention consists in improvements in or relating to colour photography. Photographic colour records of the kind which are obtained by exposing a light-sensitive halide emulsion layer through a screen of the multi-colour type or of the lenticular type, so that the record consists of minute areas recording different colours of the subject and are developed without reversal of the image, normally suffer from the disadvantage that the colours are "saddened." This "saddening" is due, it is believed, to the light passed through each screen element during exposure spreading or scattering in the sensitive layer so that the image behind one element of the screens spreads into adjacent areas which should be occupied by other colour records. "Saddening" of the colours will also occur in copies produced by printing lenticular or multi-colour screen photographs on to lenticular or multi-colour screen copy material and developing without reversal, and the copies may suffer from the cumulative effect of the spread or scatter which occurs during taking and that which occurs during copying.

Normally, photographs of the above kind are exposed during taking or printing through a transparent support (which usually bears the screen) and the extent of the spread or scatter will increase with the distance travelled through the layer from the support. The nearer the silver image is to the support therefore the less will be the detrimental effect of the spread or scatter and it is an object of the present invention to provide a process of developing photographs or prints of the above kind which will pro-

duce the image nearer to the support than is usual, and thereby reduce the degradation of the colours produced by spread or scatter.

With this object in view the invention consists in the process of developing, without reversal, photographs (originals or prints) on lenticular or multi-colour screen material as described above which is characterised by the use of a developer containing a retarder or inhibitor of development which also reacts with the emulsion layer, and as the developer diffuses through the layer loses its effective strength as to retarding or inhibiting the development at a greater rate than its loss in effective reducing strength by reason of chemical change in the developer substance, so that the developer becomes substantially more reactive, as a developer, as it diffuses through the superficial layers of emulsion towards the support. The retarder or inhibitor of development may be such as to lower the concentration of silver ions in the emulsion. Preferably the retarder or inhibitor is a solvent for silver halide which does not produce excessive fog and thiosulphates of the alkali-metals and ammonium which form stable complex salts with the silver halide are to be preferred. The proportion of thiosulphate present in the developer may be between 0.5% and 6% and normally will be less than 3% to 4%.

By the use of a developer containing a retarder or inhibitor according to the invention considerably improved colour rendering may be obtained, particularly if the developer is used for both the original and for the prints.

In carrying out the invention use is preferably made of energetic developers such as those containing metol with a caustic alkali, or amidol, or hydroquinone and the like.

Retarding or inhibiting substances

suitable for addition to the developer are, for example cyanides or thiosulphates of the alkali metals and ammonium, which form stable complex salts with the silver halide present in the emulsion layer. Other retarding or inhibiting substances such as ammonium hydroxide and thiocyanates of the alkali metals and ammonium, which do not form stable complex salts with the silver halide have not so far proved satisfactory for use in this invention, because they tend to produce excessive fog.

The invention is preferably used in developing both the original photograph (e.g. negative) and the copies (e.g. positives) from the original and examples of developers suitable for carrying out the invention are as follows:—

|    |  |               |      |      |
|----|--|---------------|------|------|
| 20 | 1. Amidol                              | - - -         | 5    | gms. |
|    | Sodium sulphite                        | (cryst) - - - | 80   | „    |
|    | Sodium tribasic phosphate              | - - -         | 20   | „    |
| 25 | Sodium thiosulphate                    | - - -         | 12.5 | „    |
|    | Water to                               | - - -         | 1000 | c.c. |
|    | 2. Metol                               | - - -         | 10   | gms. |
|    | Sodium sulphite                        | (cryst) - - - | 30   | „    |
| 30 | Sodium hydroxide                       | - - -         | 10   | „    |
|    | Sodium thiosulphate                    | - - -         | 20   | „    |
|    | Water to                               | - - -         | 1000 | c.c. |
|    | 3. Hydroquinone                        | - - -         | 4.5  | gms. |
|    | Metol                                  | - - -         | 1.5  | „    |
| 35 | Sodium sulphite                        | (cryst) - - - | 60   | „    |
|    | Sodium hydroxide                       | - - -         | 5    | „    |
|    | Sodium thiosulphate                    | - - -         | 60   | „    |
|    | Water to                               | - - -         | 1000 | c.c. |
| 40 | 4. Amidol                              | - - -         | 5    | gms. |
|    | Sodium sulphite                        | (cryst) - - - | 60   | „    |
|    | Acetone                                | - - -         | 80   | c.c. |
|    | Sodium thiosulphate                    | - - -         | 50   | gms. |
| 45 | Water to                               | - - -         | 1000 | c.c. |
|    | 5. Amidol                              | - - -         | 10   | gms. |
|    | Potassium bisulphite or metabisulphite | - - -         | 5    | „    |
|    | Sodium sulphite                        | - - -         | 40   | „    |
| 50 | Sodium thiosulphate                    | - - -         | 5    | „    |
|    | Water                                  | - - -         | 1000 | c.c. |

When using a developer according to the invention it is found that development is generally completed in about half the time required for fixation and in order to complete the fixation the photograph is therefore, in carrying out the invention, normally transferred to a fixing bath of usual kind as soon as development is complete.

Other retarders or inhibitors of development which may be added to the developer in accordance with the invention when used for developing silver bromide or iodo-bromide emulsions

(which will normally be the type of emulsion dealt with) are, for example, traces of soluble iodides or sulphides. It is thought that the iodides, by giving the silver bromide grains in the surface layers of the emulsion a superficial coating of silver iodide render them practically undevelopable, and that in percolating through the emulsion the developer is, in consequence, robbed of the small percentage of iodide used and by the time it reaches the base is capable of vigorous attack on the exposed silver bromide there. Traces of sulphides, it is believed, act similarly by the formation in the surface layers of the emulsion of silver sulphide coatings on the bromide grains.

Still further examples of the addition of a retarder or inhibitor of development to a developer is the use of potassium metabisulphite or acid potassium sulphite (potassium bisulphite) in conjunction with amidol. The potassium bisulphite (or the potassium metabisulphite) restrains the activity of the amidol as a developer but the sulphurous acid combines with the gelatine and is thus progressively removed from the developer as it percolates through the emulsion allowing the amidol to regain its activity.

The optimum proportion of retarder or inhibitor present in the developer depends to some extent upon the coating weight of the emulsion. Thus, if a thick emulsion layer is employed, the alteration in effective strength of the developer may take place in parts of the emulsion further from the base than is desired and in that case a larger proportion of retarder or inhibitor may be necessary than would be employed for a layer of normal thickness. Example 2 given above is suitable for use with a coating weight equivalent to 38 to 40 mgms. of metallic silver per square decimetre.

The substances referred to above, which in normal proportions retard or inhibit development, have the property of accelerating development when used in very small proportions, and the invention includes the use in the process of developing, without reversal, photographs on lenticular or multi-colour screen material, of a developer containing a substance which reacts with the emulsion layer and which accelerates development only when present in small proportions, the proportion initially contained in the developer being greater than that which accelerates development, and such that it is reduced as the developer diffuses through the emulsion layer by the reaction with that layer, to that which accelerates development.

The invention includes, for use in the

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process herein described, a developer containing a retarder or inhibitor of development in a proportion in relation to the quantity of developing ingredients substantially as described and predetermined to reduce colour degradation in the

manner described.

Dated this 23rd day of January, 1936.

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## COMPLETE SPECIFICATION

### Improvements in or relating to Colour Photography

I, DOUGLAS ARTHUR SPENCER, a British Subject, of 118, Fulham Road, South Kensington, London, S.W.3, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention consists in improvements in or relating to colour photography. Negative photographic colour records (and positive copies made therefrom) of the kind which are obtained by exposing a light-sensitive silver halide emulsion layer through a screen of the multi-colour type, so that the record consists of minute areas recording different colours of the subject, and are developed without reversal of the image normally suffer from the disadvantage that the complementary colour rendering is "saddened" or "de-saturated" due it is believed, to the light passed through each screen element during exposure spreading or scattering in the sensitive layer so that the image behind one element of the screen spreads into adjacent areas which should be occupied by other colour records. A further "saddening" of the colours will also occur in prints produced by printing multi-colour screen photographs which have been developed to a negative on to multi-colour screen copy material and developing to a positive as in the normal negative-positive technique since the prints will suffer from the cumulative effect of the spread or scatter which occurs during exposure of the negative and that which occurs during exposure of the copy material.

Normally, photographs of the above kind are exposed during taking or printing through a transparent support (which usually bears the screen) and the extent of the spread or scatter will increase with the distance travelled through the layer from the support. The nearer the silver image is to the support therefore the less will be the detrimental effect of the spread or scatter and it is an object of the present invention to provide a process

whereby it is possible to develop both negatives and positives of the above kind in such manner that the image is nearer to the support than is usual, and thereby reduce the degradation of the colours produced by spread or scatter.

The invention accordingly consists in the process of developing a photograph (negative or positive) on multi-colour screen material to obtain a developed image which, in the thickness of the emulsion layer, is denser nearer to the support than is obtained by the normal process of development and may increase in density as the support is approached, which comprises developing the latent image, without reversal, by the use of a developer containing a retarding or inhibiting substance which in use is gradually exhausted by forming a stable complex salt or an undevelopable silver compound with the silver halide, or by combining with the gelatine layer or by absorption thereby, the substance being initially present in proportion such that during the penetration of the developer through the emulsion layer the retarding or inhibiting effect is reduced to such an extent that the developer becomes substantially more reactive, as a developer, as it penetrates towards the support.

The retarder or inhibitor of development used in carrying out the invention may be such as to lower the concentration of silver ions in solution. Preferably the retarder or inhibitor is a solvent for silver halide which does not produce excessive fog and thiosulphates of the alkali-metals and ammonium which form stable complex salts with the silver halide are to be preferred. The proportion of thiosulphate present in the developer may be between 0.5% and 6% and normally will be less than 3% to 4% reckoned by weight on the developing solution in the case of one of normal concentration (see examples given later herein).

By the use of a developer containing a retarder or inhibitor according to the invention considerably improved colour rendering may be obtained, particularly if such a developer is used in producing

both the negative and the positive photographs.

In carrying out the invention use is preferably made of energetic developers such as those containing metol with a caustic alkali, or amidol, or hydroquinone and the like.

It has already been proposed to use silver halide solvents, such as sodium thiosulphate, in admixture with the developers used for direct development of monochrome photographs or for development of multi-colour photographs by the reversal process. In these proposals, however, as applied to direct development, the proportion of silver halide solvent has been such as to fix out the unexposed silver halide during the period required for the blackening of the exposed silver halides and has been considerably in excess of that which is used in accordance with the present invention and which is essential if the desired results are to be obtained. Further, when, in developing colour transparencies by the reversal process, thio-sulphates and other silver-halide solvents have been added to the developer for the purpose of dissolving, during the first processing, residues of undeveloped silver-halides in the fully exposed areas which would otherwise form a veil over the highlights when the transparency is subjected to the second development, in so far as the silver halide solvents are effective in producing the first image substantially nearer to the base during the negative development stage of the reversal process they are operating in an undesirable direction from the point of view of the present invention. This is because when the first image is subsequently bleached away and the residual silver halide developed to produce the final positive image the latter will be further away from the support than would otherwise be the case. The present invention is not applicable to the reversal process.

Further the silver halide solvents normally employed in the reversal processing of colour screen material, namely ammonium hydroxide and thiocyanates of the alkali metals and ammonium, do not form stable complex salts with the silver halide and have not so far proved satisfactory for use in this invention partly because they tend to produce excessive fog. The formation of this fog is not objectionable in reversal processing since the negative image and accompanying fog are destroyed during the operation of producing a reversal transparency. Moreover, in so far as ammonia and the thiocyanates when added to developers used in the reversal process are capable of

minimising the desaturation of colour produced by irradiation, they do this by a mechanism which differs in kind from that now described.

The invention is preferably used in developing both the original photograph (e.g. negative) and the copies (e.g. positives) from the original and examples of developers suitably for carrying out the invention are as follows:—

|    |                           |                   |      |      |     |
|----|---------------------------|-------------------|------|------|-----|
| 1. | Amidol                    | - - -             | 5    | gms. |     |
|    | Sodium sulphite           | (cryst) - - -     | 80   | "    |     |
|    | Sodium tribasic phosphate | - - -             | 20   | "    | 80  |
|    | Sodium thiosulphate       | - - -             | 12.5 | "    |     |
|    | Water to                  | - - -             | 1000 | c.c. |     |
| 2. | Metol                     | - - -             | 10   | gms. |     |
|    | Sodium sulphite           | (cryst) - - -     | 30   | "    | 85  |
|    | Sodium hydroxide          | - - -             | 10   | "    |     |
|    | Sodium thiosulphate       | - - -             | 20   | "    |     |
|    | Water to                  | - - -             | 1000 | c.c. |     |
| 3. | Hydroquinone              | - - -             | 4.5  | gms. |     |
|    | Metol                     | - - -             | 1.5  | "    | 90  |
|    | Sodium sulphite           | (cryst) - - -     | 60   | "    |     |
|    | Sodium hydroxide          | - - -             | 5    | "    |     |
|    | Sodium thiosulphate       | - - -             | 60   | "    |     |
|    | Water to                  | - - -             | 1000 | c.c. | 95  |
| 4. | Amidol                    | - - -             | 5    | gms. |     |
|    | Sodium sulphite           | (cryst) - - -     | 60   | "    |     |
|    | Acetone                   | - - -             | 80   | c.c. |     |
|    | Sodium thiosulphate       | - - -             | 50   | gms. | 100 |
|    | Water to                  | - - -             | 1000 | c.c. |     |
| 5. | Amidol                    | - - -             | 10   | gms. |     |
|    | Potassium bisulphite      | or metabisulphite | 5    | "    |     |
|    | Sodium sulphite           | - - -             | 40   | "    | 105 |
|    | Sodium thiosulphate       | - - -             | 5    | "    |     |
|    | Water                     | - - -             | 1000 | c.c. |     |

Although such developers as the above, containing soluble thiosulphate, have the effect of dissolving silver halides from the emulsion while development is proceeding, in order to complete the fixation it is normally necessary in carrying out the invention, to transfer the photograph to a fixing bath of the usual kind as soon as development is complete.

Although the relative proportion of the constituents is of some importance, their actual concentration is not. Thus formula 2 works practically as well if diluted five times with water. In the examples given above the developers are of normal concentration and it is in relation to such concentration that the range of 0.5 to 6% for the inhibitor has been stated. It is to be understood that for variations from normal concentrations there will be a corresponding adjustment in the proportion of the inhibitor.

Other retarders or inhibitors of develop-

ment which may be added to the developer in accordance with the invention when used for developing silver bromide or iodo-bromide emulsions (which will normally be the type of emulsion dealt with) are, for example, traces of soluble iodides or sulphides. It is known that soluble iodides react with silver bromide grains and give them a coating of or convert them completely into silver iodide which is practically undevelopable so that in diffusing through the emulsion the developer is gradually robbed of the small percentage of soluble iodide it contained and becomes capable of vigorous attack on the exposed silver bromide in the deeper layers of the emulsion. Traces of sulphides, it is believed, act similarly by the formation in the surface layers of the emulsion of silver sulphide coatings on the bromide grains.

Still further examples of the addition of a retarder or inhibitor of development to a developer are the use of potassium metabisulphite or other acid sulphite of an alkali metal (sodium bisulphite) in conjunction with amidol. Such an acid sulphite restrains the activity of amidol as a developer but free sulphurous acid is capable of combining with gelatine and of thus being progressively removed from the developer as it percolates through the emulsion with the result that the amidol increases its activity. The resulting images are not, however, so satisfactory as those obtained by the use of the preferred developers given in the above specific examples.

The optimum proportion of retarder or inhibitor present in the developer depends to some extent upon the coating weight of the emulsion. Thus, if a thick emulsion layer is employed, the alteration in effective strength of the developer may take place in parts of the emulsion further from the base than is desired and in that case a larger proportion of retarder or inhibitor may be necessary than would be employed for a layer of normal thickness. Example 2 given above is suitable for use with a coating weight equivalent to 38 to 40 mgms. of metallic silver per square decimetre.

Having now particularly described and

ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process of developing a photograph (negative or positive) on multi-colour screen material to obtain a developed image which, in the thickness of the emulsion layer, is denser nearer to the support than is obtained by the normal process of development and may increase in density as the support is approached which comprises developing the latent image, without reversal, by the use of a developer containing a retarding or inhibiting substance which in use is gradually exhausted by forming a stable complex salt or an undevelopable silver compound with the silver halide, or by combining with the gelatine layer or by absorption thereby, the substance being initially present in proportion such that during the penetration of the developer through the emulsion layer the retarding or inhibiting effect is reduced to such an extent that the developer becomes substantially more reactive, as a developer, as it penetrates towards the support.

2. A process according to Claim 1 in which a soluble thiosulphate is employed as the retarding or inhibiting substance.

3. A process according to Claim 2 in which the proportion of thiosulphate present in the developer is between 0.5% and 6%.

4. A process according to any one of the preceding claims in which a soluble iodide is used as a retarding or inhibiting substance.

5. A process according to any one of the preceding claims in which a soluble sulphide is used as a retarding or inhibiting substance.

6. A developer for use in accordance with any one of the preceding claims 1—5, substantially as given in any of the foregoing examples.

Dated this 25th day of January, 1937.

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Chartered Patent Agents.

Reference has been directed, in pursuance of Section 8, sub-section (2), of the Patents and Designs Acts, 1907 to 1932, to Specification No. 474,165.