May 28, 1940. F. F. RENWICK 2,202,026

PHOTOGRAPHIC PRINTING PROCESS AND MATERIAL

Filed March 18, 1938 4 Sheets-Sheet 1

Fig. 1.

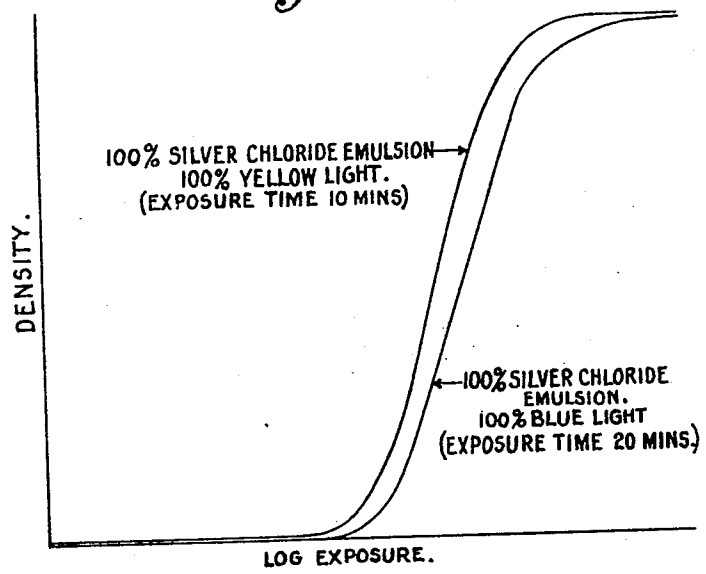
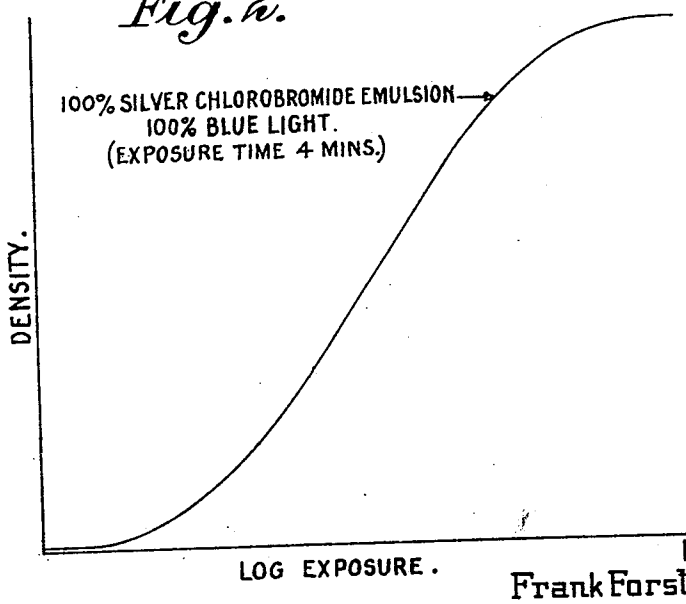


Fig. 2.



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PHOTOGRAPHIC PRINTING PROCESS AND MATERIAL

Filed March 18, 1938 4 Sheets-Sheet 2

Fig. 3.

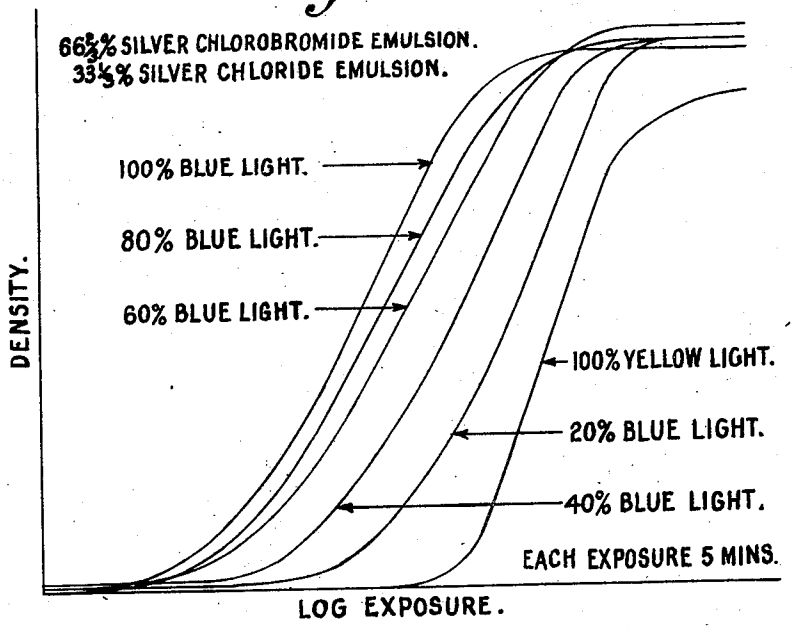
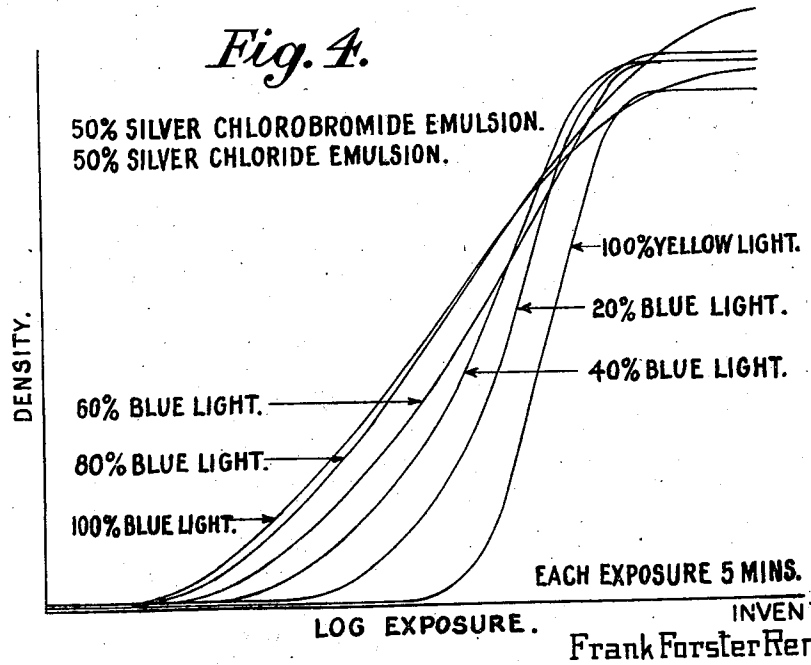


Fig. 4.



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PHOTOGRAPHIC PRINTING PROCESS AND MATERIAL

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Fig. 5.

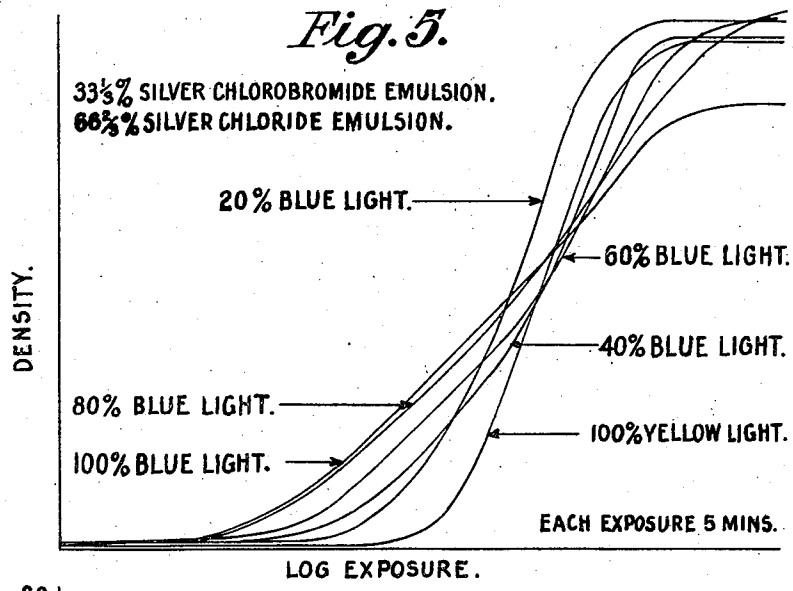
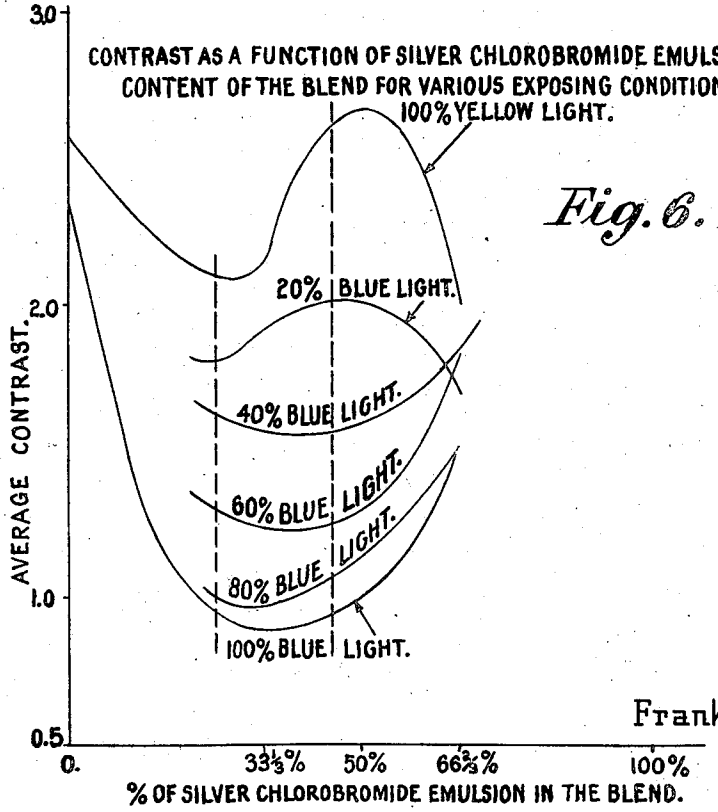


Fig. 6.



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PHOTOGRAPHIC PRINTING PROCESS AND MATERIAL

Filed March 18, 1938 4 Sheets-Sheet 4

Fig. 7

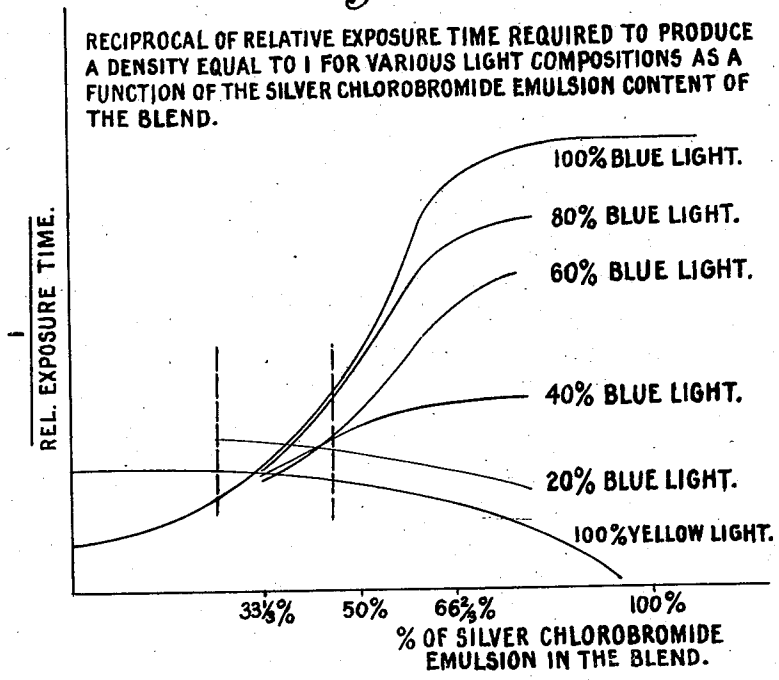
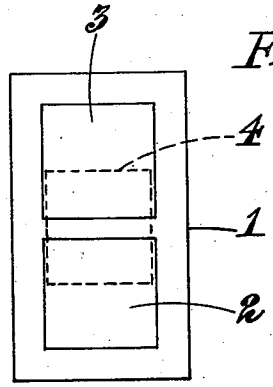


Fig. 8.



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Patented May 28, 1940 2,202,026

UNITED STATES PATENT OFFICE

2,202,026

PHOTOGRAPHIC PRINTING PROCESS AND MATERIAL

Frank Forster Renwick, Gidea Park, England, assignor to Ilford Limited, Ilford, Essex, England, a British company

Application March 18, 1938, Serial No. 196,788
In Great Britain March 18, 1937

9 Claims. (Cl. 95—7)

This invention relates to light sensitive material particularly for use in making photographic copies and to the method of using this material.

It is well known in the photographic art that the developed gradation or contrast of the silver halide emulsion coating on any particular material available may be either too steep or not steep enough to give the most pleasing or satisfactory results from a given original and leads (in such cases) to positive reproductions which are either too soft and lack vigour when the gradation is not steep enough or, if the gradation is too steep, to prints that are hard with blocked-up shadows devoid of visible detail.

In order to overcome this difficulty, it is customary at the present time to provide a large number of different grades of copy materials, e. g. sensitive papers, coated with emulsions of different gradations or degrees of contrast and to employ the grade which in the opinion of the worker is best suited to the particular negative, or the like, to be copied.

This is not an economical method as it entails the manufacture of a large number of grades of material and the holding of stocks of each grade by both manufacturers and users and the exercise of skilled judgment on the part of the worker in selecting for each negative the grade of paper best suited to his requirements.

It is an object of this invention to provide an improved method and material for producing photographic copies whereby the need for such a multiplicity of grades of copy material is largely obviated and in which the contrast of the copy can be varied at the will of the operator and the conditions of copying adjusted in such manner that a single grade of copying material can be made to produce satisfactory copies from originals of widely divergent qualities.

The invention makes use of the known facts that silver halide emulsions can be sensitised by means of dyes to spectral regions well separated from the region to which the untreated emulsion is normally sensitive and that emulsions having wide variations in their gradations may be prepared.

The invention provides light sensitive photographic material consisting of a support and coated on one side thereof a composite emulsion layer comprising two independently prepared silver halide emulsions one being a silver chloride emulsion and the other a silver bromide emulsion, the two emulsions having markedly different gradations and one being dye sensitised to light within a spectral region to which the other is substantially insensitive.

Preferably the emulsions are so selected or sensitised that each is sensitive to a spectral region to which the other is substantially insensitive and it is preferred that the two emulsions should be so selected that they are normally sensitive (i. e., without dye treatment) to as widely separated spectral regions as possible. In one convenient form of the invention the composite emulsion layer comprises a silver bromide gelatine emulsion containing a proportion of silver chloride in the form of a normal silver chlorobromide emulsion which is sensitive to the blue region of the spectrum and which may be employed without sensitizing dyes and a silver chloride gelatine emulsion of the gas light type normally sensitive to the ultra-violet and blue-violet spectral regions and which has been dye sensitised to be sensitive to the green and/or orange regions of the spectrum.

The composite emulsion layer may be prepared either by mixing the two emulsions and then casting the mixture in a single layer or the composite layer may be prepared by first coating one of the emulsions onto the support and then coating the second emulsion.

The two emulsions of the types described are readily prepared of noticeably different contrasts, particularly if the chloride emulsion is to have a steeper gradation than the bromide and by selecting a printing light of colour to which one only of the emulsions is sensitive, the gradation of a developed print on the material may be made to correspond approximately to the gradation of the emulsion affected by light of that colour. Thus if, for example, a contrasty chloride emulsion sensitised to green has been used and a green light is employed for printing, then the print will have a steep gradation while if light of a colour to which the bromide emulsion is sensitive (e. g., blue light) and to which the chloride emulsion is substantially insensitive is used then the gradation of the print will be that of the bromide emulsion which is much softer. Any desired gradation intermediate between the hard gradation of the one emulsion and the soft gradation of the other emulsion may be obtained by using a printing light of colour which will affect both emulsions in the desired proportions.

The invention accordingly includes the method of controlling the scale of gradation of the copy in a photographic copying process comprising using, for the copy, material having a composite light sensitive emulsion layer composed of two

independently prepared silver halide emulsions, one being a silver chloride emulsion and the other a silver bromide emulsion, the two emulsions having markedly different gradations and each being responsive to a spectral region to which the other is substantially unresponsive, printing by means of a printing light having actinically-useful components within each of the spectral regions of sensitivity of the two light sensitive materials and varying the relative proportions of the said actinically-useful components in accordance with the gradation desired.

The invention will now be described with reference to the accompanying drawings of which:

Figures 1 to 7 are characteristic curves relating to the particular form of material as described below by way of example and prepared in the manner set forth.

Figure 8 is a diagram illustrating the filters used for the exposure of the material.

The material was prepared as follows.

A "gas-light" emulsion of high contrast containing essentially silver chloride as the light sensitive salt was prepared and rendered sensitive to green light by the addition of one of the following dyes, the amount of dye addition being 2 ccs. of 0.05% spirit solution of dye per pound of finished emulsion (equivalent to 5.5 gms. silver nitrate). The emulsion thus sensitised is sensitive mainly to ultra-violet light and green light and only to a very much less extent to visible blue and violet light. Figure 1 shows characteristic curves (prepared as described below) of this emulsion when exposed to artificial light through a yellow filter and a deep blue filter respectively and it will be seen that it has a steep gradation. In the production of these curves the emulsion was exposed through the yellow filter for 10 minutes and through the blue filter for 20 minutes. The sensitising dye used for the emulsion must be one which does not "wander" from the grains of the emulsion to which it is added and sensitise the other with which it is mixed.

Suitable dyes are:

1.3.3-trimethyl-2'-ethyl-indoxacarbocyanine-iodide.

2,2'-diethyl-oxathiacarbocyanine-iodide.

1-phenyl-3-methyl-4-(1.3.3-trimethylindolylidene-2)-ethylidene-pyrazole-5-one.

A chloro-bromide emulsion of normal type containing silver chloride and silver bromide equivalent to 9.65 gms. silver nitrate per pound of finished emulsion and existing together in the grains was also prepared, the emulsion being sensitive to blue, violet and ultra-violet lights but not to green light. Figure 2 shows the characteristic curve (also prepared as described below) of this emulsion when exposed to blue light and it will be seen that the gradation of the emulsion is very much less steep than that of chloride emulsion. No characteristic curve of this emulsion when exposed to yellow light is given because the emulsion is substantially insensitive to light of that colour. The speed of this emulsion to blue light was about ten times the speed of the chloride emulsion to the same blue light.

The above two emulsions were separately melted, mixed in certain proportions and coated upon photographic paper base after the addition of the usual substances added for the purpose of promoting ease of coating and of handling the coated product such as ethyl-alcohol, glycerine and chrome alum.

The two emulsions were mixed in three batches in different proportions and each batch was coated separately. The proportions of the emulsions in the three batches were respectively: 33⅓% chloride emulsion to 66⅔% chlorobromide emulsion, 50% chloride emulsion to 50% chlorobromide emulsion, 66⅔% chloride emulsion to 33⅓% chlorobromide emulsion.

The three batches of materials prepared in this way were each tested by exposure for equal times behind a photographic step-wedge at a fixed distance from an illuminant consisting of a standard lamp, a transparent diffusion screen and a filter as described later, the diffusion screen acting as an extended secondary light source of substantially uniform brightness over its whole area. After exposure in this manner the materials were developed in a typical metol-hydroquinone developer for a standard time and at a standard temperature, were fixed, washed and dried. The reflection densities of the several steps on the "positive" thus obtained were measured on a photo-electric reflection densitometer and characteristic curves of the materials constructed in known manner, utilising the known transmission densities of the step-wedge which had served as a negative. The characteristic curves for the three materials obtained in this way and for different proportions of yellow and blue lights in the exposure light are shown in Figures 3 to 5.

Figure 6 is a set of curves, taken from the curves shown in Figures 1 to 5 and prepared by plotting the average contrast as a function of the silver chlorobromide emulsion content of the blend for various compositions of exposure lights. In preparing these curves, the average slope of the characteristic curves shown in the previous figures was taken between the "ends" of the curves which were considered as being at the positions where the curves reach a slope of 0.2. From these curves it will be seen that when the content of silver chloro-bromide emulsion is less than about 60% to 65% of the total, then the contrast varies progressively as the printing light is varied from 100% blue to 100% yellow. In the region between 25% and 45% of silver chlorobromide emulsion the change in contrast with change in exposure light is reasonably uniform and this range is one which, with these particular emulsions, is particularly satisfactory for practical purposes.

Figure 7 is a set of curves obtained from the curves shown in Figures 1 to 5 by plotting the reciprocal of the relative exposure required to produce a density equal to 1 on exposure to various light compositions as a function of the silver chlorobromide emulsion content of the blend. It will be seen from these curves that when the silver chlorobromide emulsion content is between 25% and 45% of the total emulsion the exposures required vary by comparatively small amounts as the colour of the printing light is varied from 100% through the blue filter to 100% through the yellow filter employed. In this particular case this range of the silver chlorobromide emulsion content is therefore useful for practical purposes when a material is desired with which the exposure time required does not vary greatly with the colour of the printing light. When the proportion of chlorobromide emulsion is about 33% the exposure required remains substantially constant as the colour of the light is varied.

Figure 8 illustrates the form given to the filters referred to above and used for varying the proportion of the yellow and blue in the exposure light. The filter consists of a plane framework

containing 2 equal rectangular apertures 2 and 3 covered respectively by a "tri-colour" blue gelatine filter and by a minus-blue or yellow gelatine filter, the framework with the attached filters being movable by a rack and pinion mechanism past the aperture 4 of the diffusion screen. The device is located between the diffusion screen and the standard lamp and by means of the device the colour of the light passing the diffusion screen and therefore operative in making the photographic exposure can be varied smoothly between wholly tri-colour blue and wholly minus-blue.

I claim:

1. Light sensitive photographic material consisting of a support and coated on one side thereof a composite emulsion layer comprising two independently prepared silver halide emulsions, one being a contrasty silver chloride emulsion and the other a silver bromide emulsion sensitive to blue light, the two emulsions having markedly different contrasts the silver chloride emulsion being dye-sensitized to light within a spectral region taken from the class consisting of green, green-orange and orange regions with a dye which does not wander from the grains of the silver chloride emulsion and sensitize the other emulsion.

2. Light sensitive photographic material consisting of a support and coated on one side thereof a composite emulsion layer comprising two independently prepared silver halide emulsions, one being a contrasty silver chloride emulsion and the other a silver chlorobromide emulsion sensitive to blue light, the two emulsions having markedly different contrasts the silver chloride emulsion being dye-sensitized to light within a spectral region taken from the class consisting of green, green-orange and orange regions, said emulsion being substantially insensitive to visible blue and violet and sensitive to ultra-violet light with a dye which does not wander from the grains of the silver chloride emulsion and sensitize the other emulsion.

3. Light sensitive photographic material consisting of a support and coated on one side thereof a composite emulsion layer comprising two independently prepared silver halide emulsions mixed together in a single gelatin emulsion layer, one being a contrasty silver chloride emulsion and the other a silver bromide emulsion sensitive to blue light, the two emulsions having markedly different contrasts and the silver chloride emulsion being substantially insensitive to visible blue and violet light but dye sensitized to green light to which the silver bromide emulsion is substantially insensitive with a dye which does not wander from the grains of the silver chloride emulsion and sensitize the other emulsion.

4. Light sensitive photographic material consisting of a support and coated on one side thereof a composite emulsion layer comprising two independently prepared silver halide emulsions mixed together in a single gelatin emulsion layer, one being a contrasty silver chloride emulsion and the other a silver bromide emulsion sensitive to blue light, the two emulsions having markedly different contrasts and the silver chloride emulsion being substantially insensitive to visible blue and violet light but dye sensitized with a dye which does not wander from the grains of the silver chloride emulsion and sensitize the other emulsion to green light and the silver bromide not colour sensitized.

5. Light sensitive photographic material consisting of a support and coated on one side thereof a composite emulsion layer comprising two independently prepared silver halide emulsions mixed together in a single gelatin emulsion layer, one being a contrasty silver chloride emulsion and the other a silver chlorobromide emulsion sensitive to blue light, the two emulsions having markedly different contrasts and the silver chloride emulsion being substantially insensitive to visible blue and violet light but dye sensitized to green light to which the silver chlorobromide emulsion is substantially insensitive with a dye which does not wander from the grains of the silver chloride emulsion and sensitize the other emulsion.

6. Light sensitive photographic material consisting of a support and coated on one side thereof a composite emulsion layer comprising two independently prepared silver halide emulsions mixed together in a single gelatin emulsion layer, one being a contrasty silver chloride emulsion and the other a silver chlorobromide emulsion sensitive to blue light, the two emulsions having markedly different contrasts and the silver chloride emulsion being dye substantially insensitive to visible blue and violet light but sensitized with a dye which does not wander from the grains of the silver chloride emulsion and sensitize the other emulsion to green light and the silver chlorobromide not colcur sensitized.

7. The method of controlling the scale of gradation of the copy in a photographic copying process comprising using, for the copy, material having a composite light sensitive emulsion layer composed of two independently prepared silver halide emulsions, one being a contrasty silver chloride emulsion and the other a silver bromide emulsion sensitive to blue light, the silver chloride emulsion being dye-sensitized with a dye which does not wander from the grains thereof and sensitize the other emulsion, the two emulsions having markedly different gradations the silver chloride emulsion being substantially insensitive to visible blue and violet but sensitive to ultra violet and to light within the spectral region taken from the class consisting of green, green-orange and orange regions, printing by means of a printing light having actinically-useful components within each of the spectral regions of sensitivity of the two light sensitive materials and varying the relative proportions of the said actinically-useful components in accordance with the gradation desired.

8. Light sensitive photographic material as claimed in claim 2, wherein the silver chlorobromide emulsion is between 25 and 45% of the total emulsion.

9. Light sensitive photographic material as claimed in claim 2, wherein the proportion of chlorobromide emulsion is about 33% of the total.

FRANK FORSTER RENWICK.

4

CERTIFICATE OF CORRECTION.

Patent No. 2,202,026. May 28, 1940.

FRANK FORSTER RENWICK.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 32, claim 6, strike out the word "dye" and insert the same before "sensitized" in line 33, same claim; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 2nd day of July, A. D. 1940.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)