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PHOTOGRAPHIC MATERIALS

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This invention relates to photographic printing material and more particularly to photographic material giving various degrees of contrast and is a continuation-in-part of my application Serial No. 387,437 filed April 8, 1941 (now U. S. Patent 2,331,660, dated October 12, 1943).

It has been known since the beginning of the use of silver chloride and silver bromide for photographic developing-out emulsions that they have widely different characteristics, of which the most striking are:

(*a*) Silver chloride is naturally more contrasty than silver bromide.

(*b*) Silver chloride develops much more rapidly (usually 20 to 40 secs.) than silver bromide (usually 1½ to 2½ mins.).

If the brightest possible print with good transparency in the shadows are required from flat negatives, it is customary to use silver chloride which is superior to silver bromide in this particular respect. On the other hand, in view of (*a*) mentioned above, very soft prints are more easily made on silver bromide paper.

It has been the practice of all photographic manufacturers for more than twenty years to sell numerous different sensitive papers.

Even as long ago as 1912 in British Specification No. 15,054, Fischer proposed to make a photographic sensitive paper by mixing or coating one over the other two emulsions giving differing contrasts under the same development conditions but with differing coloured lights for exposure. This result can be achieved by using silver chloride which as indicated above, lends itself to making a contrasty emulsion in conjunction with silver bromide which lends itself to making a soft emulsion. In fact, in an endeavour to produce such a variable contrast sensitive paper, it has been proposed by Renwick in U. S. Patent No. 2,202,026 to mix or coat in separate layers, a dye-sensitised contrasty silver chloride emulsion and an ordinary soft silver bromide or chloro bromide emulsion.

This method suffers from the serious disadvantage of giving a sensitive material which when exposed for different contrasts gives considerable inconvenience in processing. When printing most negatives which do not fall at the absolute extremes of contrast (i. e. fully soft or fully contrasty) where both emulsions come into play to varying degrees, the relation between the rates of appearance of the highlights and the heavy shadows in the same print is distorted, and moreover to add to the difficulty, differs from one negative to another. This makes it difficult to judge the development and readjust the exposure both as to amount and colour of light if it was found to be incorrect the first time. For example, we find that when printing hard and medium hard negatives on such paper the first appearances of the image are very deceptive as to what its final appearance will be, and moreover, if the exposure has been too great, say double the correct exposure, then when development is cut short in an endeavour to save the print from being wasted, the contrast obtained is much too high which would not have occurred when using ordinary single emulsion papers. Moreover, it is difficult, in fact usually impossible, to obtain a satisfactory print if development is cut short as can be done in the case of standard single emulsion papers, and which is in fact very frequently done to avoid waste when making prints. Hence the user is compelled to learn a new technique of judging the making of prints by visual inspection.

Moreover, if the emulsions are coated as superposed layers, the image which develops in the lower emulsion layer is, during development, considerably obscured by the upper emulsion layer and, as seen from above in the case of photographic paper, the highlights or shadows, whichever develop first in the lower layer are obscured and give again an unpleasant and inconvenient rate of appearance of the different parts of the image and also from one kind of negative to another, especially in the case of the large bulk of negatives which print between the extremes where both emulsions are utilised in varying degrees, all of which is of course additional to the effects already mentioned as resulting from using different halides. Hence while the use of the same halides in superposed layers overcomes some disadvantages it does not overcome all of them.

It follows that in all the above proposals difficulty is entailed in attempting to develop by inspection to say nothing of the other disadvantages referred to such as the restricted choice of convenient developing solutions and in particular I am not aware of any proposal to overcome this difficulty of inspection development.

It is an object of my invention to produce a sensitive photographic paper which is eminently suitable for development by inspection as well as having other advantages, such as ease of making a mixture which gives uniform image colours and uniform times of development over the whole range of contrasts.

According to my invention I employ a mixture of an emulsion of a silver halide which is opti-

cally sensitised to a region of the spectrum and another emulsion of the same halide but of different contrast which has its maximum sensitivity in another region of the spectrum whereby the mixture gives a difference in gradation of at least 2.5, the lowest gradation being below 1.8, by exposing to lights of different colours. I may make both emulsions of silver bromide or both of silver chloride, or even of chlorobromide, providing the halide compositions of the two emulsions are for all practical purposes the same.

I shall now refer to various forms of my invention, each of which achieves a special object.

Another disadvantage of the use of different halides is that it is not possible to make a satisfactory sensitive paper which is sufficiently highly sensitive for use in very rapidly operating machines or where only a weak light exposure is possible. According to a special form of my invention this difficulty is overcome by employing a mixture of two silver bromide emulsions.

For some purposes it is desired to make a series of prints from various negatives with a very high degree of brilliance and clarity. This was not achieved in the prior proposals of using a silver chloride emulsion mixed with a silver bromide emulsion, since the images formed in the silver chloride emulsion are more brilliant than those formed in the silver bromide emulsion.

According to another special form of my invention I achieve this object by employing a mixture of two silver chloride emulsions.

If one emulsion is sensitised to green and the other is not sensitised, such a combination cannot be processed in a yellow or yellowish-green or orange light but must be processed in the more inconvenient red light. Sometimes this does not matter, but for some purposes it is undoubtedly inconvenient. This is overcome, as well as all the disadvantages of prior proposals by a preferred form of my invention which I shall now describe.

In this preferred form which exhibits these special further advantages I employ a silver chloride emulsion which has not been specially optically sensitised, and therefore has a natural sensitivity which is high at 390 mμ with a silver chloride emulsion which has been sensitised to have its maximum optical sensitisation at about 520 mμ or less but preferably between 420 and 490 mμ, for example 470 mμ with a low natural sensitivity. When such maximum is at about 520 mμ the material can be processed in an orange light, but when it is about 470 mμ it can be processed in a relatively bright yellow.

My invention achieves a special advantage in respect of producing warm tone prints with the same developing solutions containing large quantities of a restrainer both by visual inspection and without. The use of different halides renders it extremely difficult to obtain satisfactory or at least similar brown or warm-toned prints over the whole range of contrasts. Even the use of a silver chlorobromide emulsion as proposed by Renwick does not give satisfactory warm tones over the whole range of contrasts, because he mixes it with a silver chloride emulsion, and in fact I am not aware of any prior proposals to enable such prints to be made.

I achieved this result in another special form of my invention by employing two silver chlorobromide emulsions as will be described hereinafter.

All the above methods referred to, make use of the natural sensitivity of one emulsion, hence it is important to have the other emulsion so sensitised that its natural sensitivity is sufficiently low. If the use of the natural sensitivity in this way could be avoided a wider scope would be permitted in the production of the two emulsions of the mixture. I am not aware of any prior proposal to avoid using the natural sensitivity in this way while at the same time the material can be processed in an orange or light red light. I achieve this desirable result in a preferred form of using two silver chloride emulsions in which both emulsions are optically sensitised, one with a maximum at about 470 mμ and the other at about 550 mμ with a sharp cutoff at say 580 mμ.

I shall now describe the ways of performing the several forms of my invention referred to above.

In all forms of my invention I preferably employ one emulsion which gives a gradation (measured as herein described) less than 1.8 and the other emulsion which gives a gradation of at least 2.5 greater than that of the other emulsion and of which one of such emulsions (hereafter referred to as the former emulsion) is sensitised to have its maximum speed at least 60 mμ further towards the long wavelengths than the maximum speed of the other of such emulsions, the speed of the former emulsion measured at about the wavelength of the maximum speed of the other emulsion being not greater than half the speed of the other emulsion measured at the same wavelengths, while measured at about the wavelength of maximum speed of the former emulsion the speed thereof is at least twice the speed of the other emulsion. For most purposes it is preferable that both emulsions should be substantially insensitive to wavelengths beyond 600 mμ. The said gradations are to be measured by means of light of about the wavelength (as herein defined) of maximum speed of the emulsion concerned. Where I refer herein to "about" a certain wavelength, I mean the range of wavelengths covering 40 mμ each side thereof. To ascertain the wavelength of maximum speed there should be employed a spectrogram made by using a neutral wedge with a tungsten filament at 2700° K. as the light source, and wavelengths below 390 mμ are excluded from such measurements.

By the term "silver bromide emulsion" as used herein, I mean an emulsion which consists of at least 90% of AgBr based on the total silver halide. By the term "silver chloride emulsion" I means an emulsion which consists of at least 90% AgCl based on the total silver halide.

By the term "silver-chloro-bromide emulsion" wherever used herein I mean silver-halide emulsions which contain over 10% and less than 90% (but preferably over 30% and less than 70%) of silver chloride based on the total silver halide. It is desirable that the percentage silver chloride content of the two emulsions should not differ by more than 25, but preferably not more than 10. It is the practice to add sometimes some silver iodide to silver bromide, silver chloride and silver-chloro-bromide emulsions, and such emulsions are included within the terms of the present invention.

In order to produce a sensitive photographic element of the greatest convenience and simplicity in use for most purposes (i. e. with most negatives commonly met in practice) I have found that it is preferable that the coated emulsions and the optically sensitising dye should be so chosen that the speed in the blue region of the non-optically sensitised blue sensitive emulsion should be at least 1.8 (and preferably at least twice) the speed of the optically sensitised emul-

sion in the blue region, while the speed of the optically sensitised emulsion in the green to yellow region should be between one-third and one-and-a-quarter (preferably between three quarters and one-and-a-quarter) times the speed of the non-optically sensitised emulsion in the blue region and the gradation of the non-optically sensitised emulsion in the blue portion should be between 0.8 and 1.8 (preferably between 1.0 and 1.6) while the gradation of the optically sensitised emulsion in the yellow to green region of the spectrum should be at least 2.5 greater (preferably 3.5 greater). It is usually desirable that both emulsions be substantially insensitive beyond 600 mμ.

Usually the gradation of the optically sensitised emulsion will not be more than 7.

All speeds herein referred to are measured by taking the exposure necessary to give a density of 1.0.

Whenever I refer herein to the gradation of an emulsion I mean the average slope of the characteristic H. & D. curve between densities of 0.4 to 1.6.

It is to be understood that when the emulsions are to be coated on an opaque support such as white paper, the density measurements which are made to arrive at the aforesaid measurements are to be done by reflected light.

In all measurements referred to or implied herein, development is done at 68° F. for 1½ minutes with the following solution:

Metol	grams	2.2
Na_2SO_3 cryst	do	150.0
Hydroquinone	do	17.0
Na_2CO_3 cryst	do	175.0
KBr.	do	2.8
Water	ccs	1,000

This solution is diluted with an equal part of water, for use.

Whenever I refer herein to the various characteristics (including speed and gamma) of each emulsion I mean when measured on the emulsion coated as a layer by itself at a quantity per square foot which is the same as is used for that emulsion in the composite emulsion layer.

The measurements specifically referred to as in the blue portion of the spectrum are made by exposing to a tungsten light (2700–3000° K) through a Wratten No. 47A filter, and in the green to yellow portion of the spectrum by exposing to such a tungsten light through a Wratten No. 5 filter.

Preferably the non-optically sensitised blue sensitive emulsion should be one having a characteristic H & D curve whose straight portion is as long as possible.

For the emulsion or emulsions which are optically sensitised there may be used one or more sensitising dyes, and since the emulsions are to be mixed, such dyes must be incorporated in that emulsion before it is mixed with the non-optically sensitised emulsion in such manner that after the emulsions are mixed, any tendency of the dye or dyes to wander from the one emulsion to the other is avoided or minimised for example, by adopting the procedure described in my application Serial No. 387,437. The procedure described in the co-pending application of Edward B. Knott and myself Serial No. 391,375 may be utilised in the production of the optically sensitised emulsion. Dyes having little tendency to wander are described in the co-pending application of Leslie G. S. Brooker Serial No. 321,370 filed March 1, 1940.

Example 1

For the optically sensitised emulsion a silver bromide emulsion containing 3% silver iodide calculated on the total silver halide content but free from silver chloride was prepared. To an amount of this emulsion made from 200 grams of silver nitrate there was added (at 35° C.) a mixture of 500 ccs. of ethyl alcohol containing 0.10 gram of soft lac and 200 ccs. of ethyl alcohol containing 0.03 gram of either 3-(n-heptyl)-5-[(3-methyl-2(3)thiazolinylidene) ethylidene]-rhodanine or 5[(2-ethyl-1(2)-benzoxazolylidene)-ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin. The emulsion so optically sensitised had a speed in the blue region of 2.0 with a speed in the green to yellow of 5.7 and gradation in the green to yellow of 5.5. This emulsion was allowed to stand while adding soft lac to the non-optically sensitised emulsion. This latter was a silver bromide emulsion (containing 3% silver iodide calculated on the total silver halide content but free from silver chloride) having a speed in the blue region of 5.4 and a gradation 1.5. To an amount of this emulsion made from 200 grams of silver nitrate there was added 500 ccs. of ethyl alcohol containing 10 grams of soft lac (at 35° C.). The emulsions at 35° C. were mixed and coated immediately on a paper support.

Example 2

An optically sensitised emulsion of silver bromide without any other silver halide was prepared as follows; take an amount of an emulsion giving a high gradation and made from 200 grams of silver nitrate and immediately after formation of the silver bromide there was added 0.03 gram of the second named dye of Example 1. This was ripened at 40° C. for ten minutes; then allowed to set and washed; more gelatine was added and then digested at 55° C. for 30 minutes.

The emulsion so prepared had a speed in the blue of 1.0 with a speed in the green to yellow of 2.7 and gradation in the green to yellow of 4.4.

A non-optically sensitised emulsion for mixing therewith was prepared so as to have a speed in the blue region of 4.7 and a gradation of 1.3. The two emulsions were mixed and coated immediately on a paper support.

Example 3

A bromide emulsion giving a high gradation and containing the equivalent of 200 grams of silver nitrate was adjusted to a pH of 7 and sensitised with 0.05 gram of 3-ethyl-5-(2-ethyl-1-benzoxazylidene-ethylidene)-1-phenyl-2-thiohydantoin and allowed to stand for 30 minutes at 35° C. A suspension containing 50 grams of magnesium hydroxide was then added, followed by a 5% alcoholic solution of 50 grams of soft lac resin, and then followed by addition of 50 grams of potassium chloride. The product was then kept at 35° C. until the speed of the emulsion had reached the required figure (say 90 minutes). The emulsion so prepared had a speed in the blue of 1.5 with a speed in the green to yellow of 3.0 and gradation in the green to yellow of 4.5. The same quantities of magnesium hydroxide and resin were added to a bromide emulsion to have a speed in the blue of 4.0 and a gradation of 1.2. These two emulsions were mixed and coated immediately on a paper support.

Example 4

An amount of a silver chloride emulsion was made from 200 grams of silver nitrate and immediately after formation of the silver chloride there was added 0.01 gram of the same dye as used in Example 2; then ripened at about 60° C. for about 20–40 minutes, and then more gelatine added. The emulsion so prepared had a speed in the violet of 0.06 with a speed in the green to yellow of 0.3 and gradation in the green to yellow of 5.0. There was also prepared a non-optically sensitised silver chloride emulsion containing 3% of silver bromide and 1% of silver iodide calculated on its total silver halide content and having a speed in the violet of 0.3 and a gradation of 1.5. The two emulsions were mixed in equal proportions at 30° C. and coated.

Example 5

An amount of a silver chloride emulsion was made from 200 grams of silver nitrate and immediately after formation of the silver chloride there was added 0.1 gram of the same dye as used in Example 2. This emulsion was then ripened at about 60° C. for about 40 minutes and then more gelatine added. The emulsion so prepared had a speed in the violet of 0.1 with a speed in the green to yellow of 0.8 and gradation in the green to yellow of 5.0. Also there was prepared a silver chloride emulsion in like manner except using the dye 3-n-heptyl-5(1-methyl-3-β-naphthoxazolylidene) rhodanine; this emulsion had a speed in the violet of 0.3, and in the blue of 1.1 with a gradation in the blue of 1.4. The two emulsions were mixed in equal proportions at 30° C. and coated.

Example 6

An amount of a silver chloro-bromide emulsion of 50% silver-chloride and 0 to ½% silver-iodide content (the remainder thus being silver bromide) was made from 200 grams of silver nitrate and immediately after formation of the silver halide 0.1 gram of the same dye as used in Example 2 was added. This was ripened at about 60° C. for about 40 minutes and then more gelatine added, allowed to set and washed well. The emulsion so prepared had a speed in the blue to violet of 0.2 with a speed in the green to yellow of 0.7 and gradation in the green to yellow of 5.0. There was also prepared a silver chloro-bromide emulsion of the same halide composition which was not optically sensitised but had a speed in the blue to violet of 0.8 and gradation of 1.4. These two emulsions were mixed in equal proportions at about 30° C. and coated on paper.

I claim:

1. A photographic printing material for making prints of substantially the same contrast and same density range from negatives of widely differing contrasts containing a sensitive layer comprising a mixture of two emulsions of the same silver halide, each emulsion being present in quantity sufficient to give a density of at least 1.6, at least one emulsion being optically sensitized before mixing the emulsions so that after mixing the two emulsions their maximum sensitivities lie in different spectral regions, one emulsion having in its region of maximum sensitivity before mixing a gradation of less than 1.8 over a density range of 0.4 to 1.6 and the other emulsion having in its region of maximum sensitivity before mixing a gradation at least 2.5 greater than that of the first emulsion over a density range of 0.4 to 1.6.

2. A photographic printing material for making prints of substantially the same contrast and same density range from negatives of widely differing contrasts containing a sensitive layer comprising a mixture of two silver bromide emulsions, each emulsion being present in quantity sufficient to give a density of at least 1.6, at least one emulsion being optically sensitized before mixing the emulsions so that after mixing the two emulsions their maximum sensitivities lie in different spectral regions, one emulsion having in its region of maximum sensitivity before mixing a gradation of less than 1.8 over a density range of 0.4 to 1.6 and the other emulsion having in its region of maximum sensitivity before mixing a gradation at least 2.5 greater than that of the first emulsion over a density range of 0.4 to 1.6.

3. A photographic printing material for making prints of substantially the same contrast and same density range from negatives of widely differing contrasts containing a sensitive layer comprising a mixture of two silver chloride emulsions, each emulsion being present in quantity sufficient to give a density of at least 1.6, at least one emulsion being optically sensitized before mixing the emulsions so that after mixing the two emulsions their maximum sensitivities lie in different spectral regions, one emulsion having in its region of maximum sensitivity before mixing a gradation of less than 1.8 over a density range of 0.4 to 1.6 and the other emulsion having in its region of maximum sensitivity before mixing a gradation at least 2.5 greater than that of the first emulsion over a density range of 0.4 to 1.6.

4. A photographic printing material for making prints of substantially the same contrast and the same density range from negatives of widely differing contrasts containing a sensitive layer comprising a mixture of two silver chlorobromide emulsions, each emulsion being present in quantity sufficient to give a density of at least 1.6, at least one emulsion being optically sensitized before mixing the emulsions so that after mixing the two emulsions their maximum sensitivities lie in different spectral regions, one emulsion having in its region of maximum sensitivity before mixing a gradation of less than 1.8 over a density range of 0.4 to 1.6 and the other emulsion having in its region of maximum sensitivity before mixing a gradation at least 2.5 greater than that of the first emulsion over a density range of 0.4 to 1.6.

5. A photographic printing material for making prints of substantially the same contrast and same density range from negatives of widely differing contrasts containing a sensitive layer comprising a mixture of a silver chlorobromide emulsion whose chloride content lies between 10 per cent and 25 per cent of the total halide in the emulsion and another silver chlorobromide emulsion whose chloride content lies between 10 per cent and 25 per cent of the total halide in the emulsion, each emulsion being present in quantity sufficient to give a density of at least 1.6, at least one emulsion being optically sensitized before mixing the emulsions so that after mixing the two emulsions their maximum sensitivities lie in different spectral regions, one emulsion having in its region of maximum sensitivity before mixing a gradation of less than 1.8 over a density range of 0.4 to 1.6 and the other emulsion having in its region of maximum sensitivity before mixing a gradation at least 2.5 greater than that

of the first emulsion over a density range of 0.4 to 1.6.

6. A photographic printing material for making prints of substantially the same contrast and same density range from negatives of widely differing contrasts containing a sensitive layer comprising a mixture of two silver chloride emulsions, each emulsion being present in quantity sufficient to give a density of at least 1.6, the one emulsion being optically sensitized with a maximum at about 470 mμ and the other emulsion being not optically sensitized, the one emulsion having in its region of maximum sensitivity before mixing a gradation of less than 1.8 over a density range of 0.4 to 1.6 and the other emulsion having in its region of maximum sensitivity before mixing a gradation of at least 2.5 greater than that of the first emulsion over a density range of 0.4 to 1.6.

7. A photographic printing material for making prints of substantially the same contrast and same density range from negatives of widely differing contrasts containing a sensitive layer comprising a mixture of two silver chloride emulsions, each emulsion being present in quantity sufficient to give a density of at least 1.6, the one emulsion being optically sensitized with a maximum at about 550 mμ and the other emulsion being optically sensitized with a maximum at about 470 mμ, the other emulsion having in its region of maximum sensitivity before mixing a gradation of less than 1.8 over a density range of 0.4 to 1.6 and the other emulsion having in its region of maximum sensitivity before mixing a gradation at least 2.5 greater than that of the first emulsion over a density range of 0.4 to 1.6.

8. A photographic printing material for making prints of substantially the same contrast and same density range from negatives of widely differing contrasts containing a sensitive layer comprising a mixture of two emulsions of the same silver halide, each emulsion being present in quantity sufficient to give a density of at least 1.6, at least one emulsion being optically sensitized before mixing the emulsions so that after mixing the two emulsions their maximum sensitivities lie in different spectral regions, the one emulsion having in its region of maximum sensitivity before mixing a gradation of less than 1.8 over a density range of 0.4 to 1.6 and the other emulsion having in its region of maximum sensitivity before mixing a gradation at least 2.5 greater than that of the first emulsion over a density range of 0.4 to 1.6, the one emulsion being optically sensitized to have its maximum speed at least 60 mμ further toward the longer wavelengths than the maximum speed of the other emulsion, the speed of the first emulsion measured at about the wavelength of the maximum speed of the other emulsion being not greater than half the speed of the other emulsion measured at the same wavelength, while measured at about the wavelength of the maximum speed of the first emulsion, the speed of the first emulsion is at least twice the speed of the other emulsion, both emulsions being substantially insensitive to wavelengths beyond 600 mμ.

EDWARD P. DAVEY.