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Photographic variable contrast material.

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There is described silver halide photographic black and white print material which comprises at least two silver halide emulsion components, the first of which has been spectrally sensitised so that it exhibits a log exposure range to minus blue light greater than 0.75 and to blue light less than 0.45 and the other silver halide components have a range of sensitivities to minus blue light the slowest of which is at least 0.4 Log E less sensitive to minus blue light. Preferably the slowest of which has at least 0.9 Log E less sensitivity to minus blue light.

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This invention relates to variable contrast photographic material wherein the contrast of the print obtained after exposure and processing of the silver halide emulsion layer depends on the wavelength of the light to which the emulsion layer is exposed.

The first commercially available variable contrast material were produced by ILFORD Limited following the methods set out in British Patents 494088 and 547883. In these variable contrast material is produced by combining two silver halide emulsions of which each emulsion has its own gamma value and is sensitised to a particular wavelength region of the light spectrum to which the other emulsion is not substantially sensitive. In practice one emulsion was sensitised to the blue green region of the visible spectrum and the other emulsion which is of soft contrast was not spectrally sensitised. When printing a pale magenta filter was used to yield a low contrast print and a deep yellow filter was used to yield a high contrast print. Shortly after the introduction of the ILFORD variable contrast material the Defender Photo Supply Company of the US introduced another type of variable contrast material. This was described in British Patent 547060. In this system use is made of sensitising dyes which have a preferential action on some of the silver halide particles and such sensitising dyes are used in less quantity than to produce maximum sensitivity. Thus the selected dyes impart to the emulsion a softer gradation when exposed to light within the spectral region to which the silver halide has been made sensitive than when exposed to light in the region of the spectrum to which the emulsion is naturally sensitive. But such material provides a limited contrast range because some dyeing of all the silver halide crystals occurs.

Improvements have been made in the production of variable contrast material as described in British Patent 547060 and in particular blends of emulsions having different levels of sensitisation have been employed. However in order to be able to achieve very low contrast from variable contrast material which comprises blended emulsions, when exposed to yellow or minus blue light, it is necessary for the spectral sensitivity of the emulsion component with the highest level of sensitising dye to be as high as possible in relation to the emulsion component which has not been spectrally sensitised. Unfortunately it is usually the case that spectrally sensitised emulsions tend to have a contrast at least as high as their unsensitised precursors. Thus when a blend of emulsions is exposed under conditions adjusted to provide minimum contrast, that is to say when the sensitivities of the individual emulsions of the blend show maximum separation the contrast of the most heavily dyed component of the blend will be evident as a region of high contrast over the extreme low density end of the density/log exposure characteristic curve. This results in loss of highlight detail when printing high contrast negatives.

It is the object of the present invention to overcome this problem.

Therefore according to the present invention there is provided silver halide photographic black and white print material which comprises at least two silver halide emulsion components, the first of which has been spectrally sensitised so that it exhibits a log exposure range to minus blue light greater than 0.75 and to blue light less than 0.45 and the other silver halide components have a range of sensitivities to minus blue light the slowest of which is at least 0.4 Log E less sensitive to minus blue light. But preferably the slowest of which has at least 0.9 Log E less sensitivity to minus blue light.

Preferably there are three emulsion components of different sensitivity to minus blue light the difference in the extreme being at least 0.4 Log E.

Most preferably the difference in the extreme is at least 0.9 Log E.

The three emulsion components may be called components A, B and C. Component C is the component which has been spectrally sensitised so that it exhibits a log exposure range to minus blue light greater than 0.75 and to blue light less than 0.45. Component C is the fastest component, component A is the slowest component and component B has a speed between components A and C and is dyed to provide optimal tonal response.

Typically component B has about 0.35 less sensitivity to minus blue light than component C, component A has about 0.9 less sensitivity to minus blue light than component C and A has about 0.55 less sensitivity to minus blue light than component B.

Preferably there is less of the fastest component C present in the material and most of the slowest component A.

A suitable ratio of components A, B and C by weight is 5 of A, 4 of B and 1 of C.

Preferably all the emulsion components are in the same layer but each component may be in a separate layer or the first components and one other component may be in one layer and the other components in other layers.

Thus the said first component is inherently capable of exhibiting a wide contrast range, eg, at least 1.5:1 depending on the wavelength of the light exposing source. That is to say the said first emulsion component itself is a variable contrast emulsion. When this component is present in the photographic silver halide material with at least one other emulsion component which may or may not be spectrally sensitised

there is obtained a material with a very wide contrast range that is to say at least 2:1 without excessive low density contrast under exposure conditions for low contrast. Preferably at least 3:1.

The silver halide emulsions may be prepared according to the many methods which have been employed in the photographic industry. Such methods are described in Research Disclosure Item 308119 of December 1989 and in James, Theory of the Photographic Process, 4th Edition. Methods disclosed therein include ammoniacal emulsion making, neutral or acid emulsion making. In general in these methods involve mixing a water soluble silver salt with a water-soluble halide salt in the presence of a protective colloid, and controlling the temperature during the precipitation of the silver halide.

The habit of the silver grains may be of any form used in the photographic art and includes regular cubes, octahedrons, and spherical or tabular grains. The sizes of these grains range from 0.1 to about 1 μ m.

The emulsions may be prepared using the Oswald ripening method to increase the size of the crystals during growth or the controlled crystal growth technique may be employed.

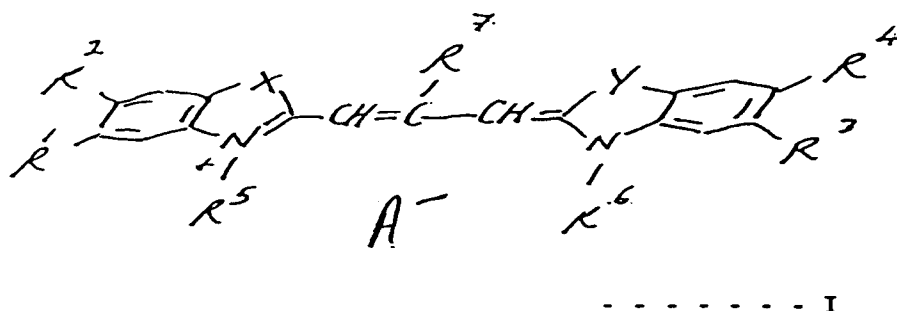
Any type of halide composition may be employed but chlorobromide emulsions are of particular use. The chloride to bromide ratio may range from 20 to 70% bromide compared with the chloride.

The emulsion for all the components may be prepared in a similar manner or different methods may be used.

A suitable emulsion for the said first component is obtained when a monodispersed silver halide emulsion is grown under conditions of constant silver ion concentration and is after desalination chemically sensitised in the presence of certain spectral sensitising dyes. The preparation of emulsions of this type are described in British Patent Specification 1335925 and in its patent of addition 1535016 wherein rhodium is incorporated into the silver halide crystals during growth.

Alternatively the said first component emulsion may be an emulsion as prepared in British Patent Specification 547060 mention of which has hereinbefore been made. If the said first component emulsion is an emulsion as prepared in B.P. 547060 then preferably this emulsion is in one layer and the other emulsion components having different sensitivities are in a separate layer or layers.

Suitable green sensitising dyes for use in the present invention are dyes of the general formula I:-



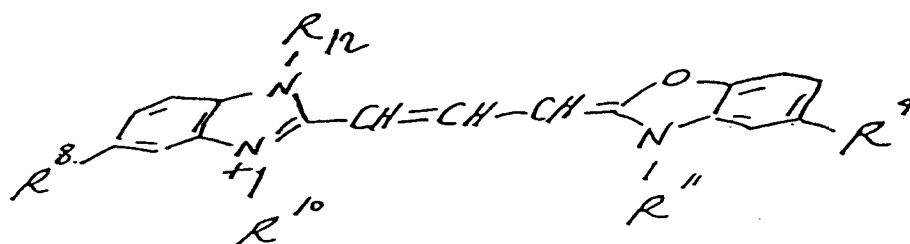
wherein X and Y are each a N-R where R is alkyl, aryl, carboxyalkyl or sulphonyl, R¹, R², R³ and R⁴ are each selected from hydrogen, alkyl, aralkyl, aryl, Cl, Br, F, oxy-alkyl, oxyaryl or CN, R⁵ and R⁶ are each alkyl, carboxyalkyl or sulphonyl, R⁷ is hydrogen, methyl or ethyl but when both X and Y are N-R then R⁷ is hydrogen and A is an anion which may be needed to balance the charge on the dye molecule.

Where alkyl is mentioned above preferably it comprises 1 to 4 carbon atoms and most preferably is methyl or ethyl.

Preferably in formula I, X is N-R, Y is O, R⁷ is hydrogen, R¹ and R² are hydrogen, Cl, CN or CF₃, R³ and R⁴ are hydrogen, alkyl aryl or oxyalkyl and R⁵ and R⁶ are all or sulphonyl.

Examples of suitable anions are iodide, bromide, tosylate and tetrafluoroborate.

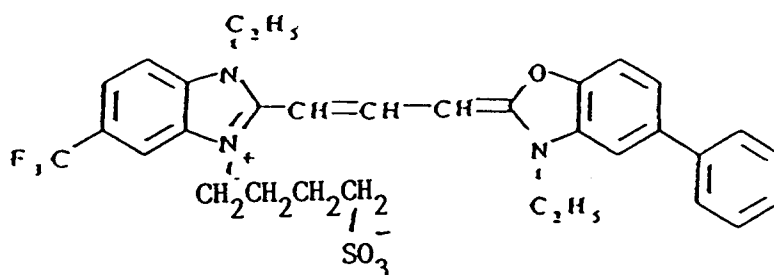
Particularly suitable dyes of formula I are dyes of formula II:-



wherein R^{12} is alkyl, R^8 is CF_3 , R^9 is aryl, R^{10} is sulphaalkyl and R^{11} is alkyl.

Preferably in dyes of formula II R^{12} is methyl or ethyl, R^9 is phenyl, R^{10} is sulphobutyl and R^{11} is methyl or ethyl.

One particular dye of formula II which is used in the examples which follow is the dye of formula III



--- III

Dyes of formula I may be prepared as described in USP 4987063 and in British Patent 1390247. A general description of the preparation of cyanine spectral sensitising dyes is given in 'Cyanine dyes and related compounds' by Hamer, published 1964.

Preferably the composition of the silver halides used both in the said first component and in the other component is substantially the same to ensure that one component does not develop more quickly than any other emulsion component and also to ensure that the image properties are the same.

All the silver halide emulsions present in the material of the present invention may be chemically sensitised with compounds such as sulphur compounds or gold compounds as described in the above cited Research Disclosure.

The binder for the silver halide grains in the material of the present invention is preferably gelatin but may be any one of the other binders described in the above cited Research Disclosure.

The silver halide emulsions used in the material of the present invention may include antifoggants, stabilisers light absorbing or reflective pigments, optical brightening agents, gelatin hardening agents coating aids as described in the above cited Research Disclosure and a blue sensitising dye to increase the inherent speed of the emulsion.

Any of the known coating techniques may be employed to coat the emulsion components on to a photographic base of the type used to prepare black and white photographic prints.

In the Example which follows a set of MULTIGRADE (registered Trade Mark of ILFORD Limited) filters marketed by ILFORD Limited was used but any other set of graded filters used to expose variable contrast photographic material can be used as can dedicated enlarger heads or even colour enlarger heads.

The exposed photographic material was developed in a MULTIGRADE photographic developing solution marketed by ILFORD Limited. This solution has the formula:-

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Potassium sulphite	15g
Hydroquinone	3.5g
Dimezone S (pyrazolidinone type developing agent)	0.3g
Potassium carbonate	10g
Potassium bromide	0.4g
Potassium hydroxide	2.5g
Benzotriazole	0.04g
E.D.T.A. (sequestering agent)	1.8g
Water to pH = 10.80	1 L
Dimezone S is the registered trade mark of Eastman Kodak.	

The following Example will serve to illustrate the invention.

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Example

Preparation and processing of comparative material. Emulsions A, B and C were all grown using an Oswald ripening step.

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Three photographic silver halide emulsions were prepared as follows:

Emulsion A: a silver chlorobromide emulsion (55% Cl, 45% Br) containing cubic crystals of size 0.49u was prepared. The emulsion was desalinated then chemically sulphur sensitized and dyes with the dye of formula III at a level of 5.2mg dye per mole of silver halide.

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Emulsion B: a silver chlorobromide emulsion (55% Cl, 45% Br, containing cubic crystals of size 0.46u was prepared. The emulsion was desalinated, then chemically sulphur sensitised and dyed with 16.7mg the dye of formula III per mole of silver halide.

Emulsion C: a silver chlorobromide emulsion (55% Cl, 45% Br) containing cubic crystals of size 0.41u was prepared. The emulsion was desalinated then chemically sulphur sensitised and dyes with 46.7mg of the dye formula III per mole of silver halide.

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Samples of each of Emulsions A, B and C were coated onto a photographic paper base and dried. The resultant coatings were then sensitometrically tested by exposure through MULTIGRADE - Grade 0 and Grade 5 filters, and processing through MULTIGRADE chemistry of the formula hereinbefore set forth.

The sensitometric results are given in Table 1

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Table 1

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	Grade 5			Grade 0		
	S0.6	LER	R1 + R*	S0.6	LER	R1 + R2*
Emulsion A	1.82	0.35	0.17	1.47	1.07	0.62
Emulsion B	1.87	0.39	0.18	2.14	0.80	0.29
Emulsion C	1.88	0.37	0.19	2.49	0.53	0.22

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* R1 = log exposure range between density 0.04 and density 0.20

R2 = log exposure range between density 0.20 and density 0.70

The three emulsions were then blended in the proportions of 10% C, 40% B and 50% A, coated on a photographic paper support and dried. The coating was sensitometrically tested as above by exposure to MULTIGRADE filters Grade 0, 3 and 5. The results are given in Table 2:

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Table 2

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Grade 5				Grade 3				Grade 0			
S0.6	LER	R1 + R2	R1	S0.6	LER	R1 + R2	R1	S0.6	LER	R1 + R2	R1
1.91	0.41	0.20	0.09	2.18	0.73	0.34	0.13	2.17	1.18	0.44	0.15

Preparation and processing of material according to the present invention.

Another silver chlorobromide emulsion (55%Cl, 45%Br) containing cubic crystals of size 0.44 μ was prepared (Emulsion D).

Following the preparation set forth in BP 1535016 to prepare a monosized silver halide emulsion which had been rhodium doped and had undergone controlled crystal growth at a constant silver ion concentration, it was desalinated, then chemically sensitised and dyed with 26.7 mg of the dye of formula III per mole of silver halide.

A sample was coated onto photographic paper base and dried. It was sensitometrically tested by exposure through MULTIGRADE Grade 0 and Grade 5 filters and processing through MULTIGRADE chemistry as hereinbefore set forth. The results are given in Table 3:

Table 3

	Grade 5			Grade 0		
	S0.6	LER	R1 + R2	S0.6	LER	R1 + R2
Emulsion D	1.87	0.38	0.23	2.49	0.83	0.44

Emulsions A, B and D were then blended in the proportions of 10% D, 40% B and 50% A, coated on photographic paper base and dried. The resultant coating was then sensitometrically-tested as above by exposure to MULTIGRADE filters Grade 0, 3 and 5. The results are given in Table 4:

Table 4

Grade 5				Grade 3				Grade 0			
S0.6	LER	R1 + R2	R1	S0.6	LER	R1 + R2	R1	S0.6	LER	R1 + R2	R1
1.94	0.39	0.18	0.08	2.16	0.75	0.41	0.18	2.12	1.27	0.57	0.28

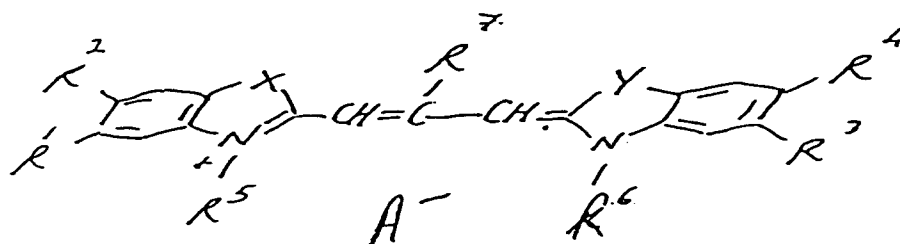
Hence, by comparison with Table 2 it can be seen that the material of the invention has a wider range of highlight contrast (R1)

Claims

1. Silver halide photographic black and white print material which is characterised in that it comprises at least two silver halide emulsion components, the first of which has been spectrally sensitised so that it exhibits a log exposure range to minus blue light greater than 0.75 and to blue light less than 0.45 and the other silver halide components have a range of sensitivities to minus blue light the slowest of which is at least 0.4 LogE less sensitive to minus blue light.
2. Silver halide material according to claim 1 characterised in that the slowest emulsion component has at least 0.9 LogE less sensitivity to minus blue light than the first component.
3. Silver halide material according to claim 1 which is characterised in that it comprises three emulsion components of different sensitivity to minus blue light, the difference in the extreme is at least 0.4 LogE.
4. Silver halide material according to claim 3 characterised in that the difference in extreme is at least 0.9 LogE.
5. Silver halide material according to claim 1 which comprises three components, the slowest component, the intermediate speed component and the fastest component has been spectrally sensitised so that it exhibits a log exposure range to minus blue light greater than 0.75 and to blue light less than 0.45.
6. A silver halide material according to claim 5 characterised in that the intermediate speed component has about 0.35 less sensitivity to minus blue light than the fastest component, the slowest component

has about 0.9 less sensitivity to minus blue light than the fastest component and the slowest component has about 0.55 less sensitivity to minus blue light than the intermediate speed component.

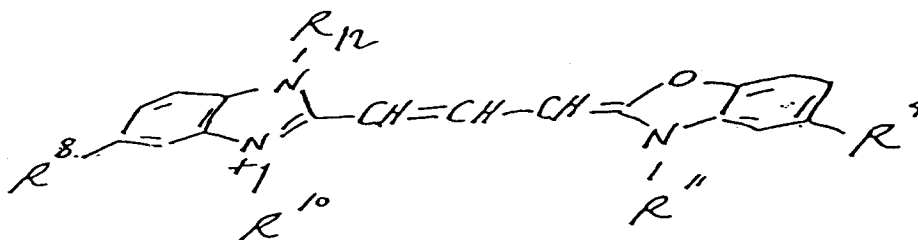
7. A silver halide material according to claim 5 characterised in that wherein the ratio of the three components by weight present in the material is 5 parts of the slowest component, 4 parts of the intermediate speed component and 1 part of the fastest component.
8. A silver halide material according to claim 1 which is characterised in that it comprises a green sensitising dye of the general formula I:-



- - - - - I

wherein X and Y are each a N-R where R is alkyl, carboxyalkyl or sulphoalkyl, R¹, R², R³ and R⁴ are each selected from hydrogen, alkyl, aralkyl, aryl, Cl, Br, F, oxy-alkyl, oxyaryl or CN, R⁵ and R⁶ are each alkyl, carboxyalkyl or sulphoalkyl, R⁷ is hydrogen, methyl or ethyl but when both X and Y are N-R then R⁷ is hydrogen and A is an anion which may be needed to balance the charge on the dye molecule.

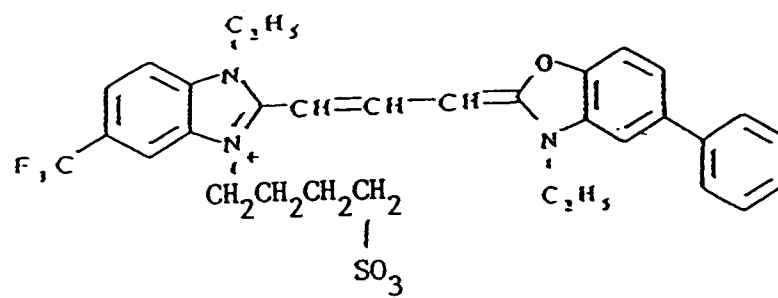
9. A silver halide material according to claim 1 which is characterised in that it comprises a green sensitising dye of the general formula II:-



- - - - - II

wherein R¹² is alkyl, R⁸ is CF₃, R⁹ is aryl, R¹⁰ is sulphoalkyl and R¹¹ is alkyl.

10. A silver halide material according to claim 1 which is characterised in that it comprises a green sensitising dye of the formula III:-



----- III