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PHOTOGRAPHIC MATERIALS

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This invention relates to the production of sensitive photographic materials such as papers, films and plates.

For certain purposes in photography, sensitive papers, films, plates and similar materials are required having two or more silver salt emulsions (in practice usually gelatino-silver-halide emulsions of course) which respond in different ways to differently coloured lights, and examples of such materials are given in British specifications Nos. 540,451, 540,464, and 544,134. In the production of these sensitive materials the emulsions are sometimes mixed before application to the support, and are sometimes applied successively in layers to the support, that is to say successively to the same side of the support, sometimes with other layers between the emulsion layers. For example, it is common practice in the production of sensitive films and plates for use in colour photography to apply successively to the support layers of emulsions sensitive to different regions of the spectrum, for instance three layers adapted to record the blue, green and red portions of the image respectively. In some cases in colour photography two or more emulsions can be mixed in one layer.

Again, multi-contrast printing papers or the like which are capable of giving a result of high or low contrast (or a constant contrast using negative of different contrast) depending on the colour of the light used in printing can be produced by applying to a paper or other support a mixture of two emulsions one of which gives an image of high contrast and can be printed by using light of one colour, and the second of which gives an image of low contrast and can be printed by light of a different colour. Instead of a mixture of the two emulsions, they can be applied successively to the paper or other support.

The different sensitivity of the emulsions to differently coloured light can be controlled by the use of sensitising dyes. Thus if two emulsions are being used in conjunction, one of them may be prepared free from dye and hence sensitive to blue light but not to light of longer wavelength, and the other may contain a dye sensitising the emulsion to yellow light, for instance, in which case the second emulsion will be sensitive to both yellow and blue light, as it possesses a natural sensitivity to blue. The emulsions will thus be sensitive to different ranges of the spectrum. Alternatively, the two emulsions may contain different dyes, so that each emulsion is dye-sensitised over a different spectral range, and in this case one of the emulsions may for instance be insensitive to light of a colour to which a second emulsion is sensitive and vice versa. Numerous dyes are known which can be used.

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In the production of photographic materials of the above type a serious difficulty arises, namely, that there is a tendency for the sensitising dye in one emulsion to "wander" (or diffuse) to a neighbouring emulsion in which its presence is not desired. If this occurs the initial difference in sensitivity between the emulsions is of course reduced, and it may even be practically lost. The tendency for a dye to wander from an emulsion containing it is very marked where the emulsion is mixed with another emulsion, and it is in such cases that the difficulty is most serious. It is also liable to be serious if the emulsions are applied successively to the support with no intervening layers between them, so that the emulsions are therefore in direct contact.

There are various ways of meeting this difficulty. Thus a dye having in itself a relatively low tendency to wander can be used, and examples of such dyes are given in British specifications Nos. 524,552 and 532,098. Furthermore, British specifications Nos. 540,451, 540,464 and 544,134 disclose that the tendency for sensitising dyes to wander from emulsions containing them can be reduced by dispersing various substances such as certain resins, resin salts and inorganic substances through the emulsions. Another method of reducing this tendency is for the dye to be incorporated in the emulsion actually during manufacture of the emulsion, in which case the dye appears to be more securely attached to the grains, although this method has certain disadvantages, for instance that the emulsion is liable to become less contrasty. There is also less chance of wandering occurring if the quantity of dye used is not greater than is necessary.

The present invention is concerned with a new method of overcoming the difficulty referred to above.

The precise mechanism by which wandering of the dye occurs when a dye-sensitised emulsion is mixed with another emulsion or is coated in a neighbouring layer is somewhat uncertain, but it seems that in some manner dye molecules which should be attached to the grains of the first-mentioned emulsion become attached to those of the second emulsion. Possibly the dye molecules actually become transferred from the grains of the one emulsion to those of the other. It is also possible that when the first-mentioned emulsion is dye-sensitised a certain number of the dye

molecules remain unattached to emulsion grains and that these molecules subsequently attach themselves to the grains of the second emulsion, so that in effect the dye has wandered from the one emulsion to the other.

It has now been found that the tendency for a sensitising dye to wander from a dye-sensitised emulsion to one or more neighbouring emulsions (which may be dye-sensitised or not) can be reduced by adding a finely divided silver halide to the first-mentioned emulsion before bringing the emulsions into association, that is to say before mixing the first-mentioned emulsion with the other emulsion or emulsions, if the emulsions are to be mixed, or coating it, if the emulsions are to be in neighbouring layers. It appears probable that in this event many of the dye molecules which might attach themselves to the grains of the neighbouring emulsions actually attach themselves to the silver halide added to the first-mentioned emulsion and hence do not have the undesirable effect they would have if they wandered to the emulsions where their presence is not desired.

The invention has the advantage that the added silver halide is removed when the photographic product is processed in the normal way and does not remain and cause a matt effect for instance. Moreover the speed of the dye-sensitised emulsion to which the silver halide is added is not materially affected. The silver halide added to the dye-sensitised emulsion can be introduced in the form of a sensitive photographic emulsion, and this is preferably of such a character or added in such a quantity that it has relatively little effect on the photographic properties of the coated photographic material eventually obtained. Thus it may be a relatively slow emulsion when compared with the other emulsions concerned, so that it does not become developable to any great degree when the coated product is exposed. Preferably it is an emulsion having grains of a size similar to those of Lippmann emulsions, the reason presumably being that the silver halide grains in such an emulsion have a larger surface area for a given weight of silver halide than is the case with other emulsions and hence for a given weight of silver halide there is probably more attraction for any available dye molecules to become attached to the grains. It is in general preferable for the silver halide to be the same as that present in the dye-sensitised emulsion to which it is added, for instance both can be silver bromide or silver chloride, but this is not essential.

The finer the grain of the added silver halide emulsion, where the silver halide is added in the form of a sensitive photographic emulsion, the less the quantity that is usually necessary, and if a certain quantity of a large grain emulsion were required then only a quarter of that quantity might be needed if an ordinarily fine grain emulsion were used, or an eighth or even less if the grains were of the size of those in Lippmann emulsions (the quantities being calculated in terms of the silver halide content). In a typical instance the quantity of the added emulsion might be 20%, 10% or less of the dye-sensitised emulsion to which it is added, in terms of the silver halide content. Again, the greater the quantity of the added emulsion that is used, the lower should usually be the threshold speed This in any event should preferably not be greater than that of the slowest of the other emulsions concerned, and it is advantageously not more than a fifth or even a tenth of the threshold speed of the slowest of the other emulsions.

The invention can be carried out simply by adding the silver halide emulsion to the dye-sensitised emulsion say fifteen minutes after the dye has been added, and then mixing the product with the other emulsion or emulsions (if a mixed emulsion is to be used) or coating it (if it is to be coated in a neighbouring layer). It also seems desirable to add a quantity of the additional silver halide emulsion to the other emulsion or emulsions to the grains of which it is desirable to reduce wandering of the dye.

It will of course be appreciated that the silver halide to be added must not have been so treated, such as by exposure to light, that it develops to silver when the coated photographic product finally obtained is exposed and developed.

The invention is illustrated by the following examples:

Example I

To 800 cc. of a contrasty gelatino-silver-bromide emulsion containing the equivalent of 20 grams of silver nitrate there was added a solution of 0.003 gram of 5 - (2 - ethyl - 1 - (2) - benzoxazolylidene - ethylidene) - 3 - heptyl - 1 - phenyl-2-thiohydantoin in 10 cc. of acetone. After 15 minutes 75 cc. of a fine grain gelatino-silver-bromide emulsion having grains of a size similar to those of Lippmann emulsions and containing 2 grams of silver bromide were added.

The product was then mixed at 30° C. with 800 cc. of a soft gelatino-silver-bromide emulsion to which 75 cc. of the fine grain emulsion had also been added.

The mixed emulsion was then coated after 30 minutes. No dye wandering was apparent on a wedge-spectrogram.

Example II

1,000 cc. of a contrasty gelatino-silver: chloride emulsion containing the equivalent of 20 grams of silver nitrate was dyed with 0.004 gram of the dye referred to in Example I. After 15 minutes there were added 100 cc. of a gelatino-silver-chloride emulsion containing 2 grams of silver chloride and slower than the emulsion to which it was added.

The product was then mixed at 25° C. with 800 cc. of a soft gelatino-silver-chloride emulsion containing the equivalent of 20 grams of silver nitrate to which 100 cc. of the second emulsion referred to in the last paragraph (which was also slower than this soft emulsion) had also been added, and the mixture was then coated after 30 minutes.

Example III

In Example I, instead of the two emulsions being mixed after the addition of the fine grain emulsion to each of them, they were applied to a support in adjacent layers.

When it is desired to reduce the tendency for the sensitising dye to wander from one emulsion layer to a neighboring emulsion layer, the additional silver halide emulsion, instead of being added to the dye-sensitised emulsion, can if desired be coated between the emulsion layers. This is of especial value where the additional emulsion has grains of a size similar to those of Lippmann emulsions, and is applicable to the production of multi-contrast materials in which the high and low contrast emulsions are coated in separate layers.

Where there is employed herein the term "neighbouring emulsion" this is used to indicate that there are two emulsions between which there is no water-impermeable layer or coating or the like.

What I claim is:

1. A process for reducing the tendency of a sensitizing dye to wander from a dye-sensitized photographic silver halide emulsion (1) to another photographic silver halide emulsion (2) in contact with the emulsion (1) comprising incorporating finely-divided silver halide grains of a size and photographic speed substantially no greater than the size and photographic speed of the silver halide grains of a Lippmann type emulsion in a fluid dye-sensitized photographic silver halide emulsion (1) containing silver halide grains which are of a size and photographic speed substantially greater than the size and photographic speed of the said finely-divided silver halide grains, and then bringing the so-treated dye-sensitized emulsion (1) into contact with another photographic silver halide emulsion (2) containing silver halide grains which are of a size and photographic speed substantially greater than the size and photographic speed of the said finely-divided silver halide grains, while at least one of the emulsions (1) and (2) is fluid.

2. A process for reducing the tendency of a sensitizing dye to wander from a dye-sensitized contrasty photographic silver halide emulsion (1) to another photographic silver halide emulsion (2) which is softer than the dye-sensitized emulsion (1) and which is in contact with the dye-sensitized emulsion (1) comprising incorporating finely-divided silver halide grains of a size and photographic speed substantially no greater than the size and photographic speed of the silver halide grains of a Lippmann type emulsion in a fluid dye-sensitized contrasty photographic silver halide emulsion (1) containing silver halide grains which are of a size and photographic speed substantially greater than the size and photographic speed of the said finely-divided silver halide grains, and then bringing the so-treated dye-sensitized emulsion (1) into contact with another photographic silver halide emulsion (2) containing silver halide grains which are of a size and photographic speed substantially greater than the size and photographic speed of the said finely-divided silver halide grains and which is softer than the dye-sensitized emulsion (1), while at least one of the emulsions (1) and (2) is fluid.

3. A process for reducing the tendency of a sensitizing dye to wander from a dye-sensitized contrasty photographic gelatino silver halide emulsion (1) to another photographic gelatino silver halide emulsion (2) which is softer than the dye-sensitized emulsion (1) and which is in contact with the emulsion (1) comprising incorporating a photographic gelatino silver halide emulsion of a Lippmann type in a fluid dye-sensitized contrasty photographic gelatino silver halide emulsion (1) containing silver halide grains which are of a size and photographic speed substantially greater than the size and photographic speed of the silver halide grains of said Lippmann type emulsion, and then bringing

the so-treated dye-sensitized emulsion (1) into contact with another photographic gelatino silver halide emulsion (2) containing silver halide grains which are of a size and photographic speed substantially greater than the size and photographic speed of the silver halide grains of said Lippmann type emulsion and which is softer than the dye-sensitized emulsion (1), while at least one of the emulsions (1) and (2) is fluid.

4. A process for reducing the tendency of a sensitized dye to wander from a dye-sensitized contrasty photographic gelatino silver bromide emulsion (1) to another photographic gelatino silver bromide emulsion (2) which is softer than the dye-sensitized emulsion (1) and which is in contact with the emulsion (1) comprising incorporating a photographic gelatino silver bromide emulsion of a Lippmann type in a fluid dye-sensitized contrasty photographic gelatino silver bromide emulsion (1) containing silver bromide grains which are of a size and photographic speed substantially greater than the size and photographic speed of the silver bromide grains of said Lippmann type emulsion, and then bringing the so-treated dye-sensitized emulsion (1) into contact with another photographic gelatino silver bromide emulsion (2) containing silver bromide grains which are of a size and photographic speed substantially greater than the size and photographic speed of the silver bromide grains of said Lippmann type emulsion and which is softer than the dye-sensitized emulsion (1), while at least one of the emulsions (1) and (2) is fluid.

5. A process for reducing the tendency of a sensitizing dye to wander from a dye-sensitized contrasty photographic gelatino silver chloride emulsion (1) to another photographic gelatino silver chloride emulsion (2) which is softer than the dye-sensitized emulsion (1) and which is in contact with the emulsion (1) comprising incorporating a photographic gelatino silver chloride emulsion of a Lippmann type in a fluid dye-sensitized contrasty photographic gelatino silver chloride emulsion (1) containing silver chloride grains which are of a size and photographic speed substantially greater than the size and photographic speed of the silver chloride grains of said Lippmann type emulsion, and then bringing the so-treated dye-sensitized emulsion (1) into contact with another photographic gelatino silver chloride emulsion (2) containing silver chloride grains which are of a size and photographic speed substantally greater than the size and photographic speed of the silver chloride grains of said Lippmann type emulsion and which is softer than the dye-sensitized emulsion (1), while at least one of the emulsions (1) and (2) is fluid.

6. The photographic material obtained by the process defined in claim 1.

7. The photographic material obtained by the process defined in claim 2.

8. The photographic material obtained by the process defined in claim 3.

9. The photographic material obtained by the process defined in claim 4.

10. The photographic material obtained by the process defined in claim 5.

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