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PHOTOGRAPHIC EMULSION

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This invention relates to the production of sensitive photographic films, plates, papers and similar materials, and is more especially concerned with the production of so-called "self-developable" photographic materials, that is to say materials which already contain photographic developing agents and which after exposure can be developed simply by treatment with an alkaline solution.

It has long been known to incorporate photographic developing agents such as hydroquinone in sensitive photographic emulsions, so that photographic plates and similar materials coated with the emulsions can be developed by means of simple alkaline solutions, but one difficulty arising in the production of such materials has been that the emulsions are unduly liable to give fogged or stained images owing to the presence of the developing agent.

One object of my invention is a self-developing sensitive photographic material which gives images free from stain.

Another object of my invention is a rapid self-developing photographic material.

Another object of my invention is a photographic material containing a developing agent having an improved degree of dispersion.

Another object of my invention is the production of stabilized emulsions by means of resinous shellac fractions.

Other objects will appear hereinafter.

According to my invention there is provided a self-developable photographic silver salt emulsion containing a photographic developing agent and having a pH of less than about 6.5. The pH should not be above about 6.9 and a preferred pH is 6.0.

The amount of developing agent dispersed in the emulsion should be sufficient to give a satisfactory image on developing a fully exposed portion of the emulsion. Such development may be done by immersion in a suitable alkaline bath. Usually the amount of developing agent, such as hydroquinone, should be more than about 3 and preferably more than 6 grams per litre of the usual type of emulsion.

When the emulsion has a pH above 7 before addition of the developing agent, the pH should first be adjusted to a value below 7, then if addition of the developing agent, such as hydroquinone, produces a lowering of the pH to say 4, it may be re-adjusted to a higher value, say 6.0 before the emulsion is coated, whereas if the addition of the developing agent, such as a para phenylene diamine base, produces a rise in the pH, it is desirable to adjust the pH either before or during the addition of the developing agent so that it never rises above 7.

Whatever the pH value improved results are obtained (especially where plates and films are being made) if a substantially water-insoluble resin is dispersed through the emulsion in addition to the developing agent. This can readily be effected by dissolving the resin in a solvent (usually ethyl alcohol, acetone or other organic solvent) and adding the solution to the liquid photographic emulsion so that the resin is precipitated to form a dispersion in the emulsion. The developing agent can be introduced into the emulsion before, during or after addition of the resin, and a good method of procedure is to employ a developing agent soluble in an organic solvent which is also a solvent for the resin and to add a solution of the two in the organic solvent to the emulsion. If desired, the resin solution can be added to a gelatine or similar solution to form a dispersion which is then itself added to the photographic emulsion, and in this case the developing agent can also be incorporated in the gelatine or similar solution, for instance by adding it to the resin solution.

The developing agent is preferably hydroquinone or a derivative thereof, although others can be used, e. g. aminophenols and phenylene diamines and derivatives thereof. Furthermore, the developing agent may be one into the molecule of which has been introduced a substituent (which may be high molecular), although the substituent should preferably not be one which greatly reduces the solubility. It is naturally preferable not to employ developers which give undue staining on account of aerial oxidation for instance; p-phenylene diamine is somewhat liable to this defect, although it can be used if there is no objection to the stain which might be produced.

It will be appreciated that a substantially water-insoluble resin is required in order that a dispersion of the resin (as distinct from a solution) can be formed in the photographic emulsion, which is essentially an aqueous liquid. Many resins, natural and synthetic, are suitable, for instance whole shellac, hard shellac, soft shellac, hydrolysed soft shellac, colophony and glyptal resins. Gum mastic, dammar, sandarach, copal, kauri and coumarone resins are also suitable, although they are not perhaps as good as those given in the last sentence. Sodium and other salts of the resins can also be used, and it is to be understood that such salts are included in the term "resins"; if, as is preferable, the final pH value of the emulsion is to be below 7, it may be necessary when using such salts (or when using other resins, for that matter) to adjust the pH value after their addition. To obtain a fine precipitate of the resin when it is added in the form of a solution in an organic solvent to the emulsion it is preferable that the concentration of the resin solution should be below about 10% in general, although this depends upon the resin

used. The advantageous effect of the resin appears to depend on the thickness of the emulsion, the greater this thickness the greater the stabilising effect of the resin. With very thin emulsions as used in certain printing papers, for instance, the effect is quite small, and in this case especially a very satisfactory product can be obtained simply by adjusting the pH value to below 7, as described above, without adding any resin at all.

It has been found that while in some cases especially where a paper support is used the presence of the resin is liable to cause a slight loss of speed, this loss can be partly at least made up by incubating the emulsion for a period of say seven days. Furthermore, an antifoggant can be incorporated in the emulsion, although this is not necessary.

The invention is applicable to self-developable emulsions in general, including those prepared from normal bromide emulsions, unwashed chloride emulsions, cinematograph positive emulsions and mixed emulsions for use in producing multicontrast printing papers as described in British Specification No. 6780/40. (Davey U. S. Serial No. 387,437, filed April 8, 1941.)

I have found that the stability of emulsions in general, whether self-developable or not and whether the pH value is above or below 7 or is exactly 7, can be increased by dispersing a substantially water-insoluble resin through the emulsion in the manner described above.

The invention is illustrated by the following examples:

EXAMPLE 1

A "self-developable" emulsion for use in coating photographic plates is prepared by adding a solution of 25–125 grams of hydroquinone (preferably 50 grams) and 50–200 grams of soft lac resin (preferably 100 grams) in 1500 cc. of ethyl alcohol (spirit) for each 100 grams of resin to 8 litres of a contrast bromide emulsion of pH value approximately 6 and containing in the 8 litres a silver content equivalent to 200 grams of silver nitrate, and then adjusting the pH value to 6.0. The ratio of lac:hydroquinone used in this example is preferably higher than one.

EXAMPLE 2

Another example of a "self-developable" emulsion is one prepared by adding a solution of 50 grams hydroquinone and 50 grams of Glyptal SB 102 resin in 750 cc. of acetone to 8 litres of a contrast bromide emulsion of the characteristics described in Example 1, and then adjusting the pH value to 6.0 as before. In general, less Glyptal SB 102 resin is required than if soft lac resin is used, and less resin is required when thin coatings of the emulsion are to be used.

EXAMPLE 3

Another example of a "self-developable" emulsion for paper coatings is one prepared by adding a solution of 200 grams hydroquinone in 500 cc. spirit to 8 litres of a bromide emulsion of the characteristics described in Example 1 and then adjusting the pH value to 6.0 as before.

If the emulsion is applied to a paper base an increased hydroquinone content is preferable on account of absorption by the base, although this absorption can be reduced by applying a resinous or other substratum to the paper before applying the emulsion.

The alkaline baths used in developing the self-developable emulsions of the invention can be of various types, and a simple solution of an alkali can be used, although the presence of sulphite is desirable to reduce any tendency to staining and that of bromide to reduce any tendency to fogging, especially if the bath is to be used repeatedly. Two suitable developing baths are given by way of example below:

Developing bath for rapid development (e. g. 5–15 seconds)

Potassium hydroxide	grams	20
Sodium sulphite	do	40
Potassium bromide	do	10
Water to make	cc.	1000

A photographic paper prepared according to the invention can be left in this bath for periods up to some minutes without substantial fogging.

Developing bath for normal development (e. g. 2 minutes)

Potassium carbonate	grams	250
Sodium sulphite	do	40
Potassium bromide	do	10
Water to make	cc.	1000

In conclusion, while the invention has been described above with reference to the use of natural and synthetic water-insoluble resins, it has also been found that there may be employed instead other water-insoluble, water-permeable colloids, for instance cellulose acetate and other cellulose derivatives.

I claim:

1. A self-developable photographic emulsion, comprising a gelatino-silver halide emulsion layer containing from about 3 to 15 grams per liter of emulsion of a photographic developing agent and having a substantially water-insoluble resin dispersed therein, and having a pH of less than about 6.5.

2. A self-developable photographic emulsion, comprising a gelatino-silver halide emulsion layer containing at least 6 grams per liter of emulsion of a photographic developing agent and having at least 12 grams per liter of emulsion of a substantially water-insoluble resin dispersed therein, and having a pH of less than about 6.5.

3. A sensitive photographic material comprising a paper support having thereon a resinous substratum over which there is a layer of a silver salt emulsion in which has been incorporated a photographic developing agent and a substantially water-insoluble resin such that the pH of the layer is less than about 6.5.

4. The method of producing a self-developable sensitive photographic material which comprises incorporating in a sensitive silver salt emulsion whose pH has been adjusted to below 7, a developing agent and a substantially water-insoluble resin so that the pH is between 5 and 6.5 and then coating such emulsion on a support and drying.

5. A self-developable photographic material comprising a support bearing a layer comprising a sensitive gelatino-silver bromide emulsion containing a substantially water-insoluble resin selected from the group consisting of soft lac resins and glyptal resins, and hydroquinone such that 8 liters of emulsion contain about 50 grams of hydroquinone and about 100 grams of the resin.

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