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PHOTOGRAPHIC SILVER BROMIDE EMULSION SENSITIZED WITH CYSTEINE

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My present invention relates to high-sensitive photographic materials for printing-out processes, particularly to positive photographic materials provided with silver bromide emulsion.

An object of my present invention consists in providing a new positive photographic material for the printing-out process which is sensitive enough to be used with the usual sources of artificial light, as, for instance, ordinary incandescent lamps.

A further object of my invention consists of a positive photographic paper, film, or plate suitable for the printing-out process and having a characteristic curve being steep enough to enable a tone reproduction which is sufficient to judge from prints made on this positive photographic material the negative from which these prints are made. Such paper, film, or plate can be used as "proof paper," "proof film" or "proof plate."

Another object of my present invention consists in making photographic material of the above described type sufficiently durable for ordinary storage conditions.

A further object of my present invention consists of a transparent positive material on which a print can be observed during its formation.

Still a further object of my present invention consists of a new photographic material enabling observation of a positive picture on a negative material without making use of the reversal process, i. e., without destroying the negative.

Still another object of my present invention consists of a printing-out photographic material suitable for the reproduction of colored pictures.

Still a further object of my present invention is to create a photographic positive material which is adapted to be used for the combined printing and viewing arrangement described and claimed in my co-pending U. S. patent application Ser. No. 393,502, filed May 15, 1941, now Patent No. 2,349,999, of which this application is a continuation-in-part.

With the above objects in view, my present invention mainly consists of a photographic silver-bromide emulsion, containing as sensitizer at least one reducing agent having a reducing power being insufficient to reduce the grains of the emulsion—either before or after exposure—in the absence of light.

The expression "silver bromide emulsion," as used throughout the specification and claims, is intended to include also silver-bromo-iodide and silver-bromo-chloride emulsions.

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Another word frequently used is the term "sensitizer"; in the following specification and claims, this expression is intended to define substances or combinations of substances which further the printing-out process of silver-halide emulsions, i. e. the blackening or coloring of silver-halide emulsions by a given amount of light, and which greatly increase the maximum density or color-intensity which is reached by prolonged exposure.

In accordance with my present invention, emulsions of the type claimed are produced by making silver bromide emulsions of very high contrast consisting of very fine grains, and by adding to this emulsion, either before or after coating, substances or combinations of substances which act as reducing agents and which are not—or only very slowly—subject to oxidation by air, and the reducing power of which is not sufficient to reduce—before or after exposure—the grains of the emulsion used in the absence of light.

I have found that many substances which are adapted to reduce the grains of silver bromide emulsions, i. e. which are adapted to act as developers at a low acidity, are powerful sensitizers for this emulsion type when used at high acidities at which they have no developing effect. It must be noted that at a low acidity these reducing substances are extremely sensitive to oxidation by the oxygen of the air, while at a high acidity they are much less sensitive. Therefore, in many cases I prefer to use as sensitizers the concentrated acid or neutral solutions of the sensitizing agents.

I furthermore found that hydroxylamine, particularly hydroxylamine hydrochloride and hydroxylamine hydrosulphate, may very well serve as sensitizer when used at sufficiently high acidities. While hydroxylamine is a developer at high values of pH, it acts as a powerful sensitizer for the printing-out process when used at a low pH with emulsions of the type mentioned above. Hydroquinone shows the same behavior although it is less suited for the purpose since it is more subject to oxidation even in acid solutions which do not act as developers.

I have furthermore found that substances containing the sulfhydryde group are especially well adapted as sensitizers of the type described: they tend to give up the hydrogen component of the sulfhydryde group, while the sulphur of two molecules is bound one to another; for this reason, these substances are very well adapted to serve as sensitizers. A substance representing an ample for the sulfhydryde group just described

is cysteine which is an extraordinarily good sensitizer for the printing-out process, e. g. if used as hydrochloride at very high acidities. Cysteine is especially well suited because the emulsions sensitized with it are very durable, the cysteine hydrochloride in this form being only very little subject to oxidation by the oxygen of the air. Besides the mentioned reaction of the sulfhydryl group, also other condensation reactions which are accompanied by the giving-off of hydrogen atoms may be used for the sensitizing of photographic emulsions for the printing-out process.

I have found that the concentration of the sensitizer is best chosen much higher than usual in photographic processes for any ingredients of silver bromide emulsions. Thus, for instance, a concentration between 10 and 40 per cent is very effective with cysteine hydrochloride as well as with hydroxylamine hydrochloride. For most of the sensitizers it is advantageous to use saturated or nearly saturated solutions.

It is possible to incorporate the sensitizer into the emulsion in the process of emulsion making, by adding it to the liquid emulsion. In some cases, however, much better results are obtained by sensitizing the emulsion after the finishing and coating process: e. g. by bathing it in a solution of the sensitizer. This is particularly advantageous because it makes possible the use of sensitizers which would attack the gelatine if added to the emulsion, but which do no or only little harm to it if properly used after coating.

I found, furthermore, that in the latter cases it is desirable to subject the emulsion to a special hardening procedure, e. g. with formalin, to make possible a treatment with the sensitizer in a very high concentration. This is necessary in order to enable the use of e. g. cysteine hydrochloride in extremely high concentration.

Even if the emulsion is especially hardened, I found it to be advantageous to carry out the sensitization of the material coated with the emulsion in a way which gives, on the one hand, full sensitizing effect while, on the other hand, it saves the gelatine layer from being destroyed or spoiled. For example, it is helpful to draw the film or paper slowly through a bath containing 20 per cent of cysteine hydrochloride at such speed and in such arrangement that the emulsion layer is in contact with the sensitizing solution for not more than 30 seconds. Generally speaking, when using a sensitizer which tends to spoil the gelatine layer, it is advisable to determine the minimum time necessary to obtain the full sensitizing effect and to use for sensitizing an arrangement by which it is ensured that this time is not appreciably exceeded.

I have also found that the water-soluble components of the human sweat represent a sensitizer of the type claimed by me if used with a silver bromide emulsion, preferably one with fine grains; my experiments have proved that thiourea contained in human sweat is its most powerful sensitizing component; however, also this substance has not such strong sensitizing effect as the human sweat itself.

In order to improve the gradation of the material, the coating of the emulsion has to be made in such a thickness that a further increase in thickness does not appreciably increase the maximum density obtained by prolonged exposure. This thickness can be easily determined, e. g. by coating a glass plate with a wedge of the emulsion to be tested and exposing it to a sufficient amount

of light, for instance, under a step-wedge, the direction of which is at right angle with that of the emulsion wedge. The resulting densities have to be judged according to the presumed use of the emulsion either with transmitted light or with reflected light, using a white background in optical contact with the emulsion or the support.

Another means to improve the contrast is the use of sensitizers, the oxidation products of which are either themselves strongly colored or give a strong color in reaction with a coupling component which may be present in the layer or which can be introduced after exposure. As an example of these sensitizers, I mention the Leuco-compounds of some dyes, e. g. of dyes containing the sulfhydryl group which show the reaction of the kind mentioned above, that is form thiocine compounds.

If it is intended to fix the pictures by dissolving the silver bromide after exposure, it is advantageous to provide for a certain amount of humidity in the emulsion layer exceeding that which is usually present in any gelatine layer. For this purpose, hygroscopic substances may be added to the emulsion, as for instance glycerine. If no complete fixing is required, the durability of the pictures can be increased to an extent sufficient for many purposes by treating the exposed layer with a de-sensitizing agent, as for instance, the so-called pinacryptol yellow. Other methods for the same purpose consist in destroying the sensitizing agent either by chemical treatment or by heat.

The use of sensitizers which yield a colored oxidation product is of advantage if fixing of the image is required, since the color of the picture is then not so strongly changed by dissolving the silver bromide.

Sensitizers which yield a colored image after exposure may be used also for making copies of color negatives. They may be used either in three separate layers which are used for prints from color separation negatives or they may be used as three superimposed layers in order to form a colored picture in one single step.

The color of pictures obtained with sensitizers, the oxidation products of which do not yield a strong color, is in the main part caused by silver particles of very small size which are chiefly surrounded by silver bromide. The ordinary fixation process removes this silver bromide which causes a strong shift in the absorption maximum of the silver particles which is accompanied by a considerable weakening of the color. In order to avoid this loss of density and contrast, it is favorable to use a toning process, e. g. the ordinary toning process with gold. An especially suitable procedure consists of a treatment with a rather concentrated, nearly colorless gold rhodanide solution which is obtained by adding gold-chloride to a hot 20 per cent ammonium rhodanide solution. This solution represents a sufficiently strong silver bromide solvent to ensure not only the toning but also the fixation of the picture. It requires, however, a very strongly hardened gelatine layer. If strongly acid sensitizers are used, as for instance cysteine hydrochloride, it is advantageous to use a neutralizing solution before the toning process takes place, or to use an alkaline toning solution.

Another way for fixing the picture or for considerably reducing its sensitivity while at the same time conserving density and contrast, consists of changing the silver bromide into a compound of high refractive index which is, however,

much less sensitive than the silver bromide, or not light-sensitive at all. An example of such a procedure is a cautious treatment of the picture with a soluble iodide, e. g. with a diluted solution of potassium iodide. Another useful procedure for the same purpose consists of destroying the sensitizer so as to leave only the relatively small sensitivity of the unsensitized emulsion, respectively an emulsion which does not assume a strong color by continued exposure. When certain kinds of sensitizers are used, this destruction can be carried out by oxidizing agents which do not destroy the silver image. In the event that certain other sensitizers, as for instance hydroxylamine hydrochloride are used, heating at a high temperature which does not destroy the picture is sufficient to destroy the sensitizer. The destroying of the sensitizer may be combined with other de-sensitizing procedures, as for instance, the treatment with ordinary de-sensitizing agents as mentioned above and/or with diluted potassium bromide solutions in order to reduce the maximum density the material is able to reach after the treatment.

If, contrary thereto, no fixing is required, it is important to make a picture of a very high contrast, taking into consideration the color of the light which is to be used in viewing the picture. If yellow or red light is to be used for this purpose, a distinct blue color of the picture is of greatest advantage. This can be produced, for instance, by keeping the paper sufficiently dry. More moisture yields a more reddish tone. With a small, controlled amount of moisture it is possible to get a reddish tone in the high-lights while a bluish tone prevails in the deep shadows. This is useful if and when much contrast is required in certain parts of the characteristic curve with the use of red light for viewing the picture.

Light-sensitive emulsions, according to my present invention, can be used with much advantage in order to get prints on surfaces of any kind whatsoever, as, for instance, on metal or wood surfaces. Either the sensitized emulsion may be spread or coated in a thin layer on the surface which is to be sensitized or the unsensitized silver bromide emulsion may be spread on the surface and the sensitizer may be added shortly before the print is to be made. This makes it possible to use also sensitizers which are strongly subject to oxidation by air. These are easily destroyed by simply heating the sensitive parts, for instance, by a hot stream of air, so that no wet procedure is required for fixing prints made in this way.

A special form of light-sensitive material according to my invention may be obtained by coating the material on the front or in the rear or on both sides with selectively absorbing layers. A light-sensitive material, for instance, as described above, arranged on a transparent base may be covered on one side by a gelatine layer which strongly absorbs red and yellow light, passing, however, most of the rays to which the material is sensitive. If an image is projected by any means on this material through the side which is coated with the colored layer, and if the emulsion has the proper degree of transparency, it will be possible to observe the formation of the image during the printing process from the other side of the material by providing a red filter between the material and the observing eye. Of course, it is advantageous to use red light as a light source for viewing in this case. The red filter, however, may be provided by simply coat-

ing the other side of the transparent material with a red layer. Generally speaking, both sides of the material can be provided with essentially complementary colored layers, one of them transmitting the light the material is not sensitive to.

Another use of the light-sensitive material as described here, is made by providing the sensitized emulsion on the rear side of an ordinary photographic film. This layer can be protected against the action of a developer by a transparent protecting layer which is not penetrable by aqueous solutions. Such layer may be removable. If a film provided with the rear-coating is developed, a positive picture on the rear-coating can be made by simply exposing the film to light with the negative layer towards the light source. This arrangement of layers can be combined with that described in the foregoing paragraph: the film base could be, for instance, of blue color and the printing-out layer on its back coated with a red protective film. It is easy to imagine similar combinations along the same line.

In order to make the material described storable, it is in some cases of advantage to eliminate catalysts promoting oxidation by adding substances which form complex compounds with such catalysts. This has been found to be helpful if, for instance, hydroxylamine is used as sensitizer.

It will be understood that each of the elements described above, or two or more together, may also find a useful application in other types of photographic silver bromide emulsions differing from the types described above.

While I have illustrated and described the invention as embodied in photographic silver-bromide emulsions, I do not intend to be limited to the details shown, since various modifications and structural changes may be made without departing in any way from the spirit of my invention.

What I claim as new and desire to secure by Letters Patent is:

1. A photographic silver-bromide emulsion containing cysteine.
2. A photographic silver-bromide emulsion containing cysteine hydrochloride.
3. A photographic silver-bromide emulsion containing an acid solution of cysteine.
4. Method of sensitizing a photographic silver-bromide emulsion including the steps of first coating a photographic base with said photographic silver-bromide emulsion and finishing the same; and thereafter sensitizing said thus applied and finished silver-bromide emulsion with cysteine.
5. Method of sensitizing a photographic silver-bromide emulsion including the steps of first coating a photographic base with said photographic silver-bromide emulsion and finishing the same; and thereafter bathing said thus applied and finished silver-bromide emulsion in a solution of cysteine.
6. Method of sensitizing a photographic silver-bromide emulsion including the steps of first coating a photographic base with said photographic silver-bromide emulsion; hardening the surface of said thus applied silver-bromide emulsion; and thereafter sensitizing the thus hardened surface of said silver-bromide emulsion with a highly concentrated cysteine hydrochloride solution.

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