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PROCESS FOR THE DIRECT PRODUCTION OF POSITIVE PHOTOGRAPHIC IMAGES

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This invention relates to a process for the direct production of positive photographic images and to photographic material used for such a process.

It is known that photographic layers produced from silver chloride emulsions are blackened without previous exposure to actinic light in photographic developers, if the latter contain no potassium bromide. The reduction of silver chloride to silver is already strongly inhibited by the addition of small amounts of potassium bromide to a developer (only a few mg./l. will do to bring about this effect). It has now been observed that sensitivity of this reaction can considerably be increased by adding to the silver chloride materials traces of such substances as act as nuclei for development, for instance, colloidal noble metals or noble metal compounds difficultly soluble in water, as, for instance, colloidal silver, colloidal gold, silver sulfide etc. The quantities used hereof amount to about 0.01–0.5 g./l. of emulsion. If, besides traces of such substances as acting as nuclei for development, small amounts of a silver bromide emulsion of higher sensitivity are added to a silver chloride emulsion and the layers obtained are exposed according to the sensitivity of the silver bromide emulsion, on the subsequent development in a soda sulfite solution free from potassium bromide and containing developing substances, such as metol or hydroquinone, the following reaction takes place: the exposed silver bromide is reduced to silver, bromide ions corresponding to the amount of reduced silver being formed thereby. The bromide ions prevent the exposed areas from being fogged, i. e. they prevent a reduction of the silver chloride to silver. Silver bromide at the non-exposed areas is not reduced by the developer. No bromide ions are formed at these areas, so that reduction of the silver chloride proceeds smoothly. At the exposed areas, therefore, only as much silver is formed as corresponds to the reduced bromide; as only very small amounts of silver are concerned, slight blackening only which is scarcely visible is produced, i. e. these areas after processing are practically white if the light-sensitive layer was cast onto paper, or they are transparent if the layer was cast onto a transparent base. At the non-exposed areas, however, silver chloride representing the chief constituent of the layers is reduced, so that these areas show a very deep blackening. So the exposed areas of these layers remain light whereas the non-exposed ones become dark, i. e. a direct positive image of the object is obtained by one process. In order to remove the non-developed silver halide, the developed images have still to be fixed, washed and dried. It is also feasible to modify the process in such a manner that negative silver is removed by using known reducers so that positive silver only is left. This method allows one to obtain direct positives with excellent whites.

The proportion of silver chloride to silver bromide depends on the kind of emulsions used and lies in the range of between 0.1–10 grams of silver bromide to 100 grams of silver chloride. The preparation of these emulsion layers can also be performed in such a manner that

by the addition of small amounts of potassium bromide or potassium iodide to a silver chloride emulsion such direct positives yielding layers are obtained. The process, however, is not limited to mixtures of silver chloride and silver bromide. As low sensitive silver salts, besides silver chloride, also other silver salts, such as silver oxalate, silver stearate, silver ferrocyanide etc., can be used, in which case silver chloride may find application as the higher sensitive component. As higher sensitive silver salts, besides silver bromide, also silver iodide may be used. It is an essential feature of the new process that the emulsion used in a small amount exhibits a higher sensitivity to light and a lower solubility in the photographic developers used than the less sensitive component. The process can also be modified in such a maner that the less sensitive and higher sensitive components of the mixture consists of mixtures of silver salt emulsions of different gradations. It is also possible to optically sensitize the more sensitive emulsion and to subsequently expose same behind a suitable light filter. Furthermore, known toning substances as well as stabilizers, for instance, mercapto benzothiazole, wetting agents etc., may be added to the layers thus obtained.

For achieving a good definition power of these photographic layers the addition of products such as those listed below to these layers has proved to be of advantage to prevent or retard a diffusion of the dissolved silver salts. For this purpose there may be used, for instance, high molecular products, such as polyacrylic acid, polyvinyl alcohol, polyvinyl pyrrolidone, and compounds containing long carbon chains, such as stearic acid residues. Also hardening of gelatin by means of well known products, for instance, formalin, shows a useful effect.

The composition of the developer has a considerable influence on the aforesaid process. These solutions are to develop the higher sensitive emulsion before the silver chloride is dissolved and reduced. The same chemicals are generally used which find application for the usual photographic processes, however, without potassium bromide that, for instance, for the silver chloride-silver bromide system can be replaced by sodium chloride. Furthermore, for carrying out the new process, the presence of a silver halide solvent, for instance, sodium sulfite, is required. The silver halide dissolving effect of alkaline sulfite solutions can be increased by the addition of known compounds, for instance, sodium thiosulfate, organic amines etc. Also the developers employed for fine-grain development, for instance, p-phenylene diamine and derivatives thereof, possess a sufficiently strong dissolving power of silver chloride and other silver salts so that when using such substances the addition of further silver halide solvents can sometimes be dispensed with.

It has been found that when using certain developing solutions the addition of small amounts of potassium bromide generally not exceeding 50 milligrams per litre has a useful effect on development. Such addition, in comparison with the amounts of potassium bromide used in photographic developers, is so small that the developers used according to the present invention can be considered to be practically free from potassium bromide.

The process for the production of direct positive images according to the present invention shows the advantage that processing can be performed in the same way as in the case of a usual negative process without any additional processing steps. If the developer is appropriately composed development proceeds extraordinarily fast that being of advantage, for instance, for automatic, photographic processes. The fact that the silver separated from the dissolved silver chloride is highly fine-grained and opaque allows one to produce especially thin reverse layers with a very small amount of silver. A

coating of less than 1 gram of silver per square meter is generally sufficient for this purpose. In consequence thereof, fixing takes a few seconds only so that the new process is especially suited for quick developments. The new process is also of great importance for X-ray photography. The sensitivity of the aforesaid reactions is extraordinarily high so that already such actions of light as cause only a scarcely visible blackening upon the usual negative layers yield a distinct positive. Silver images obtained according to the present invention may be subjected to any after-treatment known in photography, for instance, intensification, reduction, toning etc. They may also be used for the contact hardening process and other processes known in the art. It is also feasible to modify the process in such a manner that the differently sensitive emulsions are cast in separate layers and the multilayer materials are worked up into direct positives by means of the above described developers.

Many specific objects, features and advantages of the present invention will become apparent to those skilled in the art from the specific examples appearing below. The following examples are not to be considered as limiting the invention but are merely illustrative of methods of carrying it out.

Example 1

To a silver chloride emulsion prepared according to known methods are added per litre 10 cc. of a silver bromide emulsion the sensitivity of which being about twice or three times as high as that of the silver chloride emulsion, and 0.1 gram of colloidal silver. The mixture of emulsions is cast as usual onto paper, film or glass, the silver content of the layer amounting to about 1 gram of silver per square meter. After exposure development is performed in the following solution:

Water	cc	1000
Metol	grams	3
Soda	do	30
Sodium sulfite anhydrous	do	30
Temperature	°C	18

Already after 30 seconds a positive image of the object is obtained. As in the case of the usual photographic processes the developed positive is stopped in 2 per cent acetic acid, fixed, washed, and dried. As the silver bromide emulsion any silver bromide emulsion prepared in the usual manner which is fit for the intended use may be employed. Sensitivity and gradation of the positives depend on the corresponding properties of the employed silver bromide emulsion. These layers generally exhibit a higher sensitivity to light than a negative prepared by means of a silver bromide emulsion only. Therefore, on using silver bromide emulsions of very high sensitivity to light for obtaining these mixed emulsions a material is obtained which is capable of recording extraordinarily weak actions of light.

Example 2

To a silver chloride emulsion prepared according to known processing methods are added per litre 20 cc. of a silver bromide emulsion the sensitivity of which being a hundred times higher than that of the silver chloride emulsion, and 0.3 gram of colloidal gold. The mixture of these emulsions is applied in such a thin layer that the silver coating amounts to about 0.5 gram per square meter only. These layers can be hardened by adding formalin or other known substances and coated with a protective layer of gelatin to which, if desired, some colloidal silver is added. Development of this layer is carried out in the following solution:

Water	cc	1000
Metol	grams	1
Hydroquinone	do	3
Soda	do	60

Sulfite anhydrous	do	120
Potassium bromide	do	0.05
Temperature	°C	18

Already after 15 seconds a completely developed positive is obtained; owing to the very small coating thickness a fixing time of a few seconds will do. As the developing and fixing time can still essentially be shortened by raising temperature of the solutions such layers are especially suited in combination with suitable apparatus for a fast production of directive positives.

Example 3

To a silver chloride emulsion of very low speed produced according to known recipes are added 500 cc. of a silver chloride-bromide emulsion of low sensitivity which has orthochromatically been sensitized with known dyestuffs, and 0.1 gram of colloidal silver. This emulsion is applied to paper as usual and developing is carried out in the following solution:

Water	cc	1000
Metol	grams	3
Soda	do	20
Sodium sulfite anhydrous	do	30
Sodium chloride	do	0.5
Temperature	° C	18

Such layers which only slightly differ as to sensitivity of the employed silver halide emulsions are preferably exposed behind a yellow filter as the yellow light only reacts upon the orthochromatic silver chloride-bromide emulsion. Such layers are suitable, for instance, for producing photographic prints.

Example 4

To a silver chloride emulsion prepared according to well known processes are added per litre besides 0.2 gram of colloidal silver sulfide, 1 gram of potassium bromide or 1 gram of potassium iodide dissolved in water, a small amount of the silver chloride being converted thereby to silver bromide or silver iodide respectively. Such layers can be exposed as usual and a direct positive of brown image-color is obtained in a solution of the following composition:

Water	cc	1000
p-Phenylenediamine	grams	3
Soda	do	5
Sodium sulfite anhydrous	do	1
Temperature	° C	18

Developing time about 2–4 minutes.

Example 5

To 1000 parts of an emulsion of silver ferrocyanide obtained by precipitating a silver nitrate solution with an equivalent amount of potassium ferrocyanide in the presence of gelatin, which exhibits only a very low light sensitivity, are added per litre 20 cc. of a silver chloride emulsion and 0.3 gram of colloidal silver. These layers directly yield a positive on developing in the following solution:

Water	cc	1000
Metol	grams	2
Soda	do	20
Sodium sulfite anhydrous	do	10
Temperature	° C	18

Developing time 60 seconds.

In this way layers can be produced which possess a low light-sensitivity only.

Example 6

To a silver chloride emulsion prepared according to known processes are added per litre besides 0.02 gram of colloidal silver, 15 cc. of a fine-grained silver bromide emulsion the sensitivity of which is 30 times as high as that of the silver chloride emulsion which has ortho-

chromatically been sensitized as usual. In order to obtain layers with a high resolving power, 5–10 grams of the sodium salt of 2-stearylamino-5-7-disulfonic acid are added to the foregoing mixture. The emulsion is cast onto a support which is equipped with an antihalation layer in a rather small coating thickness. Development is carried through in the following solution:

Water	cc	1000
Metol	grams	0.5
Hydroquinone	do	3
Soda	do	10
Sodium sulfite anhydrous	do	10
Temperature	° C	18

Developing time about 1 minute.

In this way layers are obtained which are suitable for making reductions (microfilms).

The present invention for the production of direct positive images is not only suited for the processing methods as described in the Examples 1–6 but may generally be employed wherever the production of photographic positives or duplicate-negatives is required. Whereas, for instance, according to the above described processing methods gelatin has been used as a binder, it is also feasible to modify the process in such a manner that other binding agents but gelatin may find application, for instance, synthetic high molecular products such as sericose (partially hydrolized acetylcellulose), polyvinyl alcohol, hydroxy groups containing copolymerizates, collodion and other products used for this purpose in photography.

The new process may also be used for the production of printing matrices. A further field of application for the present invention is color photography, where it may be utilized, for instance, for the known methods according to the silver-dye-bleach process, the process of color development, the toning process, for the screen plate and other additive color processes, for the production of monochrome as well as of polychrome images. The various possibilities which are open to the new process shall be further explained in the following.

The new process has proved to be especially suitable for the direct production of photographic positive images when using other binding agents than gelatin. It is known that high sensitive silver bromide emulsions cannot easily be obtained in other binding agents other than gelatin, for instance, in synthetic high molecular products. On the other hand, however, it is comparatively easy to produce silver chloride emulsions or other silver salt emulsions of comparatively low sensitivity by means of such binding agents. As according to the new process for the direct production of positive images, besides the main portion of silver chloride only very small amounts of a high sensitive silver bromide emulsion are required, these small amounts of a high sensitive silver bromide emulsion prepared as known in the art by means of gelatin as binding agent can be added to a silver chloride emulsion precipitated in any synthetic high molecular compound which is suited for photographic processes, for instance, sericose, polyvinyl alcohol etc. The gelatin containing emulsion is preferably diluted with water or with another solvent, for instance, acetone-water-mixture. Such layers give sensitivities which are essentially higher than those of the hitherto known emulsions on the base of the non-gelatinous binding agent. If emulsions of lower sensitivity are to be obtained it may be of advantage to precipitate also the higher sensitive emulsions, for instance, the silver bromide emulsion in another binding agent. The following example serves for illustrating this process:

Example 7

10 grams of silver nitrate dissolved in a mixture of acetone and water (1:1) and subsequently 3.5 parts of sodium chloride dissolved in 15 cc. of water are added to 1000 parts of a 4 per cent sericose solution in acetone-water (2:1) (sericose=partly hydrolized acetyl cellulose), a finely grained silver chloride precipitate being obtained thereby. The excess salts can be removed by precipitating the silver chloride carrying sericose with water. After washing the sericose is redissolved with an acetone water mixture and there are added 0.03 gram of colloidal silver and 10 cc. of a high-sensitive silver bromide emulsion prepared in the usual manner with gelatin as binding agent and diluted with 30 cc. of water and 20 cc. of acetone. This solution is cast onto paper or film and after exposing in accordance with the sensitivity of the silver bromide emulsion is developed at a temperature of 18° C. for 30 seconds in the following solution:

Water	cc	1000
Metol	do	2
Sodium sulfite anhydrous	do	30
Soda anhydrous	do	25

If the new process is to be used for the production of photographic positives which are to be used as printing matrices, the following possibilities are given:

Small amounts of a higher sensitive silver bromide emulsion and traces of colloidal silver sulfide as developing nuclei are added, for instance, to a silver chloride emulsion of comparatively low sensitivity and the layer thus obtained is developed after exposing in a developer which is free from potassium bromide, a direct positive being obtained thereby. The gelatin of this positive can be tanned at the silver-containing places with a solution of bichromate and can thus be rendered absorbable for fat-soluble colours. The layer can also be hardened by development in a sulfite-free pyrocatechol developer and the non-hardened gelatin can be washed off with hot water. For the latter process no sulfite as a silver chloride solvent must be added to the developer as this would prevent the hardening, but in this case sodium thiosulfate or other solvents, for instance, ammonium salts or organic amines, are used. According to the same principle also wash-out reliefs with dyed layers can be produced for monochrome or polychrome images. The following example is to illustrate the production of printing matrices according to the new invention.

Example 8

To a silver chloride emulsion prepared as known in the art are added per litre 0.02 gram of colloidal silver sulfide and 15 cc. of a higher light-sensitive silver bromide emulsion and the mixture thus obtained is coated in the usual manner on a suitable support. After exposure the layer is developed in the following solution:

Water	cc	1000
Metol	grams	2
Soda	do	30
Sodium sulfite anhydrous	do	25
Temperature	° C	18

Developing time 40 seconds.

The positive thus obtained is fixed, washed and converted in the following solution into a printing relief:

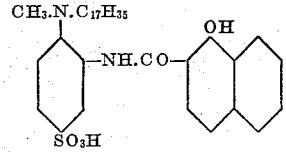
Water	cc	1000
Potassium bichromate	grams	5
Copper sulfate	do	15
Potassium bromide	do	10

The application of the new invention for the direct production of photographic color positives shall be described for the process of the chromogen development while using color formers which are fast to diffusion. As light-sensitive emulsion a mixture is used of a comparatively light-non-sensitive, non-sensitized silver chloride emulsion with small amounts of a higher sensitive silver bromide emulsion sensitized with dyestuffs corresponding to the red- or green-sensitive layer of a multilayer material. To this emulsion are added in the usual manner small amounts of such products as acting as

developing nuclei, for instance, colloidal silver, colloidal gold etc. and a color former which is fast to diffusion. Such color formers for the chromogen development have been disclosed in patents. For this purpose, for instance, components of azomethine- or indophenol dyestuffs may be used which carry solubilizing acid groups and residues of higher alphatic hydrocarbons, of natural resins, of polypeptides or hydroaromatic hydrocarbons etc. These emulsions are cast in the usual manner in superposed layers, interposing a yellow filter between the upper, only blue-sensitive layer and the lower green- and red-sensitive layers. After appropriate exposure adapted to the sensitivity of the silver bromide emulsion these layers are treated in a developer containing, for instance, p-phenylene diamine or its derivatives which, with the color couplers contained in the layers, yields a dyestuff. These substances have the property to dissolve silver chloride to a considerable extent so that only very small amounts of sodium sulfite need to be added to these developers in order to initiate a direct positive development. The color-forming developer reduces the exposed silver bromide, bromide ions being set free thereby. The latter prevents at these places a reduction of the dissolved silver chloride which, therefore, is reduced to silver only at the non-exposed places, the corresponding dyestuffs being simultaneously formed thereby. Whereas the developing substances suitable for the present invention reduce silver chloride very fast, this process proceeds considerably more difficultly and slowly in the case of silver bromide. If, therefore, very small amounts of another developing substance of higher reducing power which is not suitable for color formation, for instance metol, are added to such a color-forming developer, reduction of silver bromide is essentially due to this substance; in this case, no oxidation product is formed which with the color coupler present in the layer would give a dyestuff, i. e. the weak negative resulting from the silver bromide consists of silver only and contains no dyestuff. On the other hand, reduction of silver chloride which is present in much bigger quantities is essentially due to the color-forming developer the oxidation product of which gives the dyestuffs desired with the color couplers. After developing and intermediately washing the small amounts of negative silver and the larger amounts of silver formed by the reduction of silver chloride are dissolved by means of known products, for instance, potassium ferricyanide or converted into silver salt which are removed by subsequent fixations. The process is suited for the production of high sensitive, negative as well as positive photographic material. The following example shall further illustrate this process.

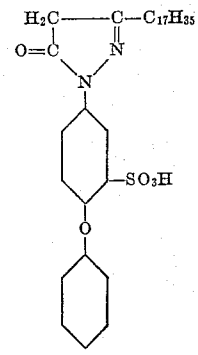
Example 9

To a silver chloride emulsion prepared as known in the art are added per litre 0.1 gram of colloidal silver and 12 cc. of a higher sensitive silver bromide emulsion which is sensitized with known dyestuffs for the red- or green-sensitive layer respectively. The emulsion mixture containing the silver bromide emulsion sensitized for the red light and per litre 20 grams of a compound of the following formula as a coupler for the cyan dyestuff image:

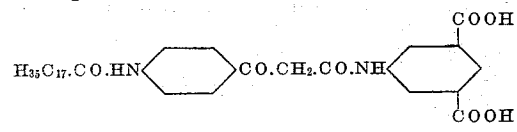


is first coated onto paper, glass or film. Upon this layer there is coated the corresponding green-sensitive emulsion mixture to which are added as a purple color

coupler per litre 20 grams of a compound of the following formula:



After coating a yellow filter layer prepared as known in the art as intermediate layer a mere blue-sensitive emulsion mixture is used for providing the upper layer. To this emulsion mixture are added per litre 20 grams of a compound of the following formula:



which on development gives a yellow dyestuff. After exposure these layers are treated at 18° C. for 40 seconds in the following developer:

Water	cc	1000
Diethyl-p-phenylene diamine hydrochloride	grams	3
Metol	do	0.05
Sodium sulfite anhydrous	do	3
Soda	do	4

The further processing of the images is done as known in the art. A positive three-color image is thus obtained.

I claim:

1. A process for the production of photographic images using a photographic material comprising, in contact with each other in at least one layer, a spontaneously developable silver salt emulsion which is developable under ordinary developing conditions in a special silver salt developing solution without previous exposure to actinic light and a light sensitive silver halide emulsion which, only after exposure to actinic light, is developable in said special developing solution to a negative image, said latter silver halide emulsion being of higher light sensitivity than said spontaneously developable silver salt emulsion, the proportion of the higher light-sensitive silver salt to the spontaneously developable silver salt lying in the range between about 0.1 to 10 grams of the higher light-sensitive silver salt to about 100 grams to the spontaneously developable silver salt which comprises exposing said material to an object to be reproduced such that only the higher light sensitive silver salt emulsion is affected by the exposing light and developing said exposed material in said special developer, the latter being an ordinary silver salt developing solution containing as solvent an agent which has a higher dissolving power for the lower than for the higher light sensitive silver salt and containing salts having the same anions as those of said higher light sensitive silver salt at most in such a quantity that the reduction of said spontaneously developable silver salt emulsion is not prevented until the developing solution forms an extremely faint negative image in the silver halide emulsion, and forms a conspicuous positive image in the spontaneously developable emulsion, the non-metallic by-products from the faint negative image effectively inhibiting the spontaneous development of a conspicuous positive image in the spontaneously developable emulsion in those areas having the negative image whereby a conspicuous direct positive image is developed.

2. A process according to claim 1 wherein the higher

light sensitive silver salt amounts to no more than 10 per cent of the weight of the spontaneously developable silver salts present in said photographic material.

3. A process according to claim 1 wherein a photographic material is used, the spontaneously developable silver salt emulsion of which contains substances selected from the group of reduction nuclei and substances forming reduction nuclei with dissolved silver salts said reduction nuclei being capable of catalysing the reduction of silver halide emulsions to silver by photographic developing solutions without exposing said emulsions containing said reduction nuclei to actinic light.

4. A process according to claim 1, wherein the silver salts of the spontaneously developable emulsion consist mainly of silver chloride and those of the more light sensitive emulsion mainly of silver bromide.

5. A process according to claim 1, wherein the higher light sensitive emulsion contains at least one optical sensitizer.

6. A process according to claim 1, wherein the binding agents of the silver salt emulsions comprise substances retarding the diffusion of dissolved silver salts.

7. A process according to claim 1, wherein the spontaneously developable emulsion and the silver halide emulsion are contained in separate layers which are in contact with each other.

8. A process according to claim 2, wherein the spontaneously developable silver salt emulsion contains substances selected from the group of reduction nuclei and substances forming reduction nuclei with dissolved silver salts.

9. A process according to claim 2, wherein the silver salts of the spontaneously developable emulsion consist mainly of silver chloride and those of the light sensitive emulsion mainly of silver bromide.

10. A process according to claim 2, wherein the higher light sensitive emulsion contains at least one optical sensitizer.

11. A process according to claim 2, wherein the negative silver image is removed by treating the negative and the positive image with a silver solvent until the silver of the negative image has dissolved.

12. A process according to claim 2, wherein the development takes place in the presence of a color coupler for the color forming development, and the photographic developer is a color forming developer.

13. A process according to claim 3, wherein the reduction nuclei are substances selected from at least one of the group of colloidal noble metals and noble metal compounds difficultly soluble in water.

14. A process according to claim 13, wherein the reduction nuclei are colloidal silver.

15. A process according to claim 13, wherein the reduction nuclei are colloidal silver sulfide.

16. A process according to claim 8, wherein the silver salts of the spontaneously developable emulsion consist mainly of silver chloride and those of the more light sensitive emulsion mainly of silver bromide.

17. A process according to claim 8, wherein the higher light sensitive emulsion contains at least one optical sensitizer.

18. A process according to claim 12, wherein mixtures of said higher and lower light sensitive silver salt emulsions are applied in at least two superimposed layers on a single support, the more light sensitive emulsions of the layers being sensitive to different regions of the spectrum, each layer containing a color coupler for the production of a dyestuff different from that of the neighboring layer.

19. A process according to claim 12, wherein the photographic developer contains a mixture of a color forming and a small amount of a non-color forming developer.

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