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DEVELOPMENT PROCESS AND DEVELOPER
FOR PRODUCING HARDENED IMAGES
UPON EXPOSED SILVER HALIDE-COLLOID
EMULSIONS

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It is known that developing solutions comprising alkali and trihydroxybenzene (pyrogallie acid), or some dihydroxybenzenes such as hydroquinone, chlorhydroquinone, pyrocatechine, cause a hardening of the emulsion colloid at the exposed and developed places if the usual addition of sulphite to the developing solution is considerably reduced or entirely suppressed. This phenomenon may be explained by the fact that with the development the substances contained in the developer give rise to the formation of a tannic acid as a product of oxidation which is adsorptively fixed by the emulsion colloid, which is of course formed in larger proportion at those places where a more intensive reduction of silver halide to metallic silver occurs. The said developing solutions which are free from sulphite or poor in sulphite may therefore be used to develop and harden images in an exposed emulsion layer which images in many respects correspond to those obtained by the exposure of chromate colloids.

However, in actual practice the use of the hardening developers very often gives rise to difficulties such as on the one hand washing away the layer and on the other hand this layer becoming entirely insoluble, and the causes thereof could not be explained up to the present. Insolubility of the layer is for instance caused by oxidation of the developing substance in the air during the development to tannic acid; the otherwise usual addition of sulphite in order to avoid a too fast oxidation cannot be used in the present case, for by addition of small quantities the conservation is not sufficient and by addition of larger quantities no hardened image is formed. Those drawbacks form a bar against the technical use of the hardening developers.

According to the invention the drawbacks of the washing away of the layer and also the layer becoming insoluble are removed by the simultaneous employment of trihydroxybenzene (pyrogallie acid) and a dihydroxybenzene, e. g. pyrocatechine in the same developer or successively with the same developing process, and a hardened image is obtained which practically corresponds to the best hardened chromate gelatine images viz. they show a tanning exactly corresponding to the reacting quantities of light, or to the quantities of silver reduced during development. This result could never be obtained by following the known processes.

The action obtained with a solution of different developers (pyrogallie acid and different dihydroxybenzenes such as hydroquinone, pyrocatechine, chlorhydroquinone etc.) upon exposed silver halide colloid emulsions is not at all of the same nature as that obtained with solutions of other chemicals (particularly alkalis) which solutions have for the remainder a suitable composition, the latter showing very marked differences in action which manifest themselves for instance in that a pyrogallie acid developer also readily hardens the non-exposed portions of the emulsion, whereas the dihydroxybenzenes e. g. pyrocatechine, even leave exposed portions sometimes unhardened, so that portions of the emulsion which are perceptibly darkened, do not resist washing with warm water. The practical result of this phenomenon resides for instance with the silver bromide pigment process in which detail in the lighter portions of the image is washed away. Now for good results the compensation of the antagonistic properties of these developers is obtained by the combined developer according to the invention.

Moreover the described combination has proved to be particularly suitable in those cases in which the penetration of the active light with exposure, and of the hardening developer into the emulsion with the development, ought to occur from different sides, for instance with films exposed from the back.

The technical conditions are the following: The developer penetrating into the layer first comes into contact with substantially non-exposed emulsion and only by further penetration comes upon exposed portions in a progressive manner. Therefore, an essentially different hardened image is obtained with a pure pyrocatechine alkali developer (as for instance proposed by Koppmann in German Patent 309,193) than with the pyrogallie acid-pyrocatechine mixture according to the invention. Since with a pure pyrocatechine developer (according to German Patent 309,193) a hardening occurs at all exposed portions of the image, which hardening resists washing with warm water, this hardening viewed from the exposed side, penetrates very far into the layer. Often it will be found that the hardening on the opposite side from the side of exposure of the layer is more intensive than at the side of exposure proper, although naturally the larger quantity of light must have acted upon the side of exposure. This seems to be due to the fact, that simultaneously with the hardening of the gelatine its perviousness to the pure pyrocatechine developer is reduced. In some cases

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this reduction may proceed so far as to prevent the hardening, even with development for a prolonged period, to penetrate into the other side of the layer. This causes the image during the subsequent treatment with warm water to be entirely or partially washed away, or it causes the formation of an insoluble film which entirely or partially grows together with the developed hardened relief.

10 This phenomenon does not present itself with the mixture of a dihydroxybenzene and trihydroxybenzene according to the invention. With such a mixture, on the contrary, the highest degree of hardening of all portions of the image is present at the point acted upon by the largest quantity of light and consequently at the side of exposure. It may be accepted that this hardening in accordance with the reacting quantity of light is due to a better penetrating ability of the developing mixture of the new composition.

20 With the same composition of the developer the developing and hardening capacity of the pyrogalllic acid is considerably higher than that of any dihydroxybenzene. It consequently appears that, as a rule, the proportion of trihydroxybenzene in the developer according to the invention ought to be smaller than the proportion of the dihydroxybenzene namely in the ratio of 1:5 or 1:30. With a suitable pyrogalllic acid pyrocatechine developer the ratio of pyrogalllic acid to pyrocatechine is for instance 1:15. If the relative percentage of pyrogalllic acid is increased the action proceeds farther into the layer but also the solubility of the non-exposed portions of the layer decreases. If the relative percentage of pyrogalllic acid is reduced the properties of the pyrocatechine dominate. Consequently the properties of the developing mixture may be controlled at will in connection with the purpose for which the hardened image is to be employed.

40 A further important improvement is obtained by considerably reducing the usual addition of alkali which highly promotes oxidation. The usual mixture applied for instance with Koppmann's process (so called Jos-Pe-process) comprises about ten times more parts by weight of potash than of pyrocatechine. On the other hand for instance developers are recommended with a ratio of 1 part by weight of pyrocatechine to 7.5 parts by weight of potash. Other proposals go in the same direction. In any case the proportion of the alkali carbonates contained in hardening developers has always been taken considerably larger than the proportion of the usually employed pyrocatechine or other compounds which act in a like manner. However, with all these formulas it appears that the developing mixture which is to be prepared immediately before use is highly oxidized during the normal developing period. In addition thereto the danger of insolubility arises, which is obviated by the invention, according to which the proportion of potash to be added for instance to the above described pyrogalllic acid-pyrocatechine developer or to the usual pyrocatechine developer is at the utmost equal to the proportion of pyrocatechine and preferably in the ratio of 1:2 to 1:2.5. It is evident that instead of potash other alkalis may be used, in which event the proportion thereof is to be calculated in accordance with their alkalinity with respect to the proportion of potash mentioned as unit.

70 For instance 0.84 part by weight of sodium carbonate corresponds to 1 part by weight of potash etc. Likewise it is possible to replace the pyro-

catechine by other suitable developers. A developing mixture with reduced percentage of alkali contains for instance about 2.5 parts by weight of pyrocatechine, 1 part by weight of potash and different proportions of water depending upon the purpose for which the developer is to be used, for instance 150 parts by weight of water and if desired an addition of pyrogalllic acid. With this developer faultless hardened images can be obtained for instance for use in etching for intaglio printing and the developing mixture which is to be prepared directly before use faultlessly prevents the layer being washed away and also this layer becoming insoluble.

15 With the application of the described process it is not imperatively necessary to mix the stock solutions of the developer and the alkali; it is rather advantageous to apply in the sense of the inventive idea a developing process in which the layer to be developed is first treated in a known way with a bath of one solution until it is soaked therewith and then with the other solution, if desired with a third solution in which the development is completed. As a normal layer of emulsion can absorb only restricted proportions of liquid and as a smaller proportion of alkali is used as developer the first bath is preferably an alkaline bath. Its alkali content depends upon the absorbing properties of the emulsion with respect to liquids or upon the thickness of the layer of the emulsion respectively.

20 A potash content of 25 per cent (or a corresponding ratio of other alkalis for instance 20 per cent of caustic soda) appears to be generally suitable. The concentration of the second bath (containing the developer composed of pyrogalllic acid and a dihydroxybenzene in the proportions previously given) or of a second bath of pyrocatechine and a third bath of pyrogalllic acid is of minor importance. This concentration may be chosen at will but with weaker concentration the development should be prolonged. The described embodiment in which separate baths are applied has the advantage that as a matter of course an oxidation of the developer present in the bath only can take place in the second bath, further that only very small proportions of alkali come into contact with a continually fresh proportion of the developer in the second bath and that the contact between alkali and developing substance is most lasting in the depth of the layer to be developed. This process causes a pronounced development in the depth. It is particularly suitable if the latent image is present in the depth of the layer (for instance with films exposed from the back) and if fogging and consequently the formation of a film at the upper side of the layer is to be avoided.

45 In the above description the developing substance pyrocatechine has only been mentioned as an example. Making allowance for the different developing capacities of the different developing substances previously mentioned, any other developing dihydroxybenzene, such as hydroquinone or chlorhydroquinone may be used with pyrogalllic acid in performing the process.

I claim:—

1. The process for effecting a hardening development of latent photographic images upon silver halide emulsions comprising: developing and hardening said emulsion in a solution consisting of five to thirty parts of a dihydroxybenzene capable of developing exposed silver halide emulsions to one part of pyrogalllic acid 75

and an alkali accelerator in water, the ratio of the alkali to the developer content being not greater than one to one by weight when measured in terms of potassium carbonate.

5 2. A process for effecting a hardening development of latent photographic images upon silver halide emulsions comprising: treating the said emulsion in an alkali accelerator, then developing the latent image in an aqueous solution consisting
10 of five to thirty parts of a dihydroxybenzene capable of developing exposed silver halide emulsions to one part of pyrogalllic acid.

3. A hardening photographic developer consisting of five to thirty parts of a dihydroxybenzene
15 capable of developing exposed silver halide emul-

sions to one part of pyrogalllic acid, and an alkali accelerator in water, the ratio of the alkali to the developing substances being not greater than one to one when measured in terms of potassium carbonate.

4. A hardening photographic developer consisting of an aqueous solution of a dihydroxybenzene capable of developing exposed silver halide emulsions, a trihydroxybenzene and an alkali accelerator, the ratio of the alkali accelerator to the
10 developing substances being not greater than one to one when measured in terms of potassium carbonate.

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