

ALIEN PROPERTY CUSTODIAN

DEVELOPMENT OF PHOTOGRAPHIC LAYERS

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The invention relates to a method of developing photographic silver halide layers and consists in that adsorptive oxidation-reduction systems are used as developers, the reduction potential of said systems being electrolytically influenced during the development.

According to the new method, it is not only possible to maintain the developing power of the developer permanently at the stage desired in each particular case; but the effectiveness of the developer and thus also the γ -value of the developed silver halide layer can be influenced. This influencing is of technical importance, particularly for maintaining a definite γ -value during the development of picture strips.

It is recognised that the use of reversible oxidation-reduction systems is essential for the new method of development.

As suitable oxidation-reduction systems the following may be mentioned by way of example: anthraquinones, phenanthraquinones, indophenols, aminoindophenols, indamines, thiazines, oxazines, safranines, rosindulines, rosindones and vlogenes, but also conjugated systems with open chains, such as iso-vitamin C, heterocycles such as indigo derivatives, organic complexes of the type $\text{Alk}_z[(\text{R.COO})_y \text{Me}_z]$ in which

$\text{Alk} = \text{K}, \text{Na}, (\text{NH}_4^+)$ etc.

$\text{Me} = \text{Fe}, \text{V}, \text{Ti}, \text{Cr}$ etc.

$\text{R} =$ the organic radicals

$-\text{CH}^z, -\text{CH}^z\text{OH}, -\text{COO} \dots, -\text{CH}^z.\text{COO} \dots, -\text{C}^0\text{H}^z, \text{C}^0\text{H}^z.\text{O} \dots$ etc.,

and x, y and $z =$ represent the various valency stages. Examples of such organic complexes are the ferric complexes with citrates. These oxidation-reduction systems constitute a mixture of the oxidation and reduction products, the designation of the oxidation-reduction systems always being effected according to the oxidized form. According to the invention, such an oxidation-reduction system is used as developer, and the reduction potential desired in each particular case, which, of course, can be altered from case to case, is electrolytically adjusted.

If, for example, it is desired to maintain the reduction potential at a constant value during the development, in order thus also to obtain a constant γ in the developed halogen silver layer, the developer is in each particular case reduced by the electrolysis in the degree in which it is oxidized by the development.

Essential for the new mode of working is the use, in the first instance, of reversible sys-

tems as developers, inasmuch as only in this manner can the equilibrium be permanently maintained or be influenced in the desired sense. The usable oxidation-reduction systems must be adsorbed upon the silver halide grains or latent image.

Furthermore, it is advisable to use only those oxidation-reduction systems which yield a constant potential. As experience shows, this is best ensured in the fields which do not lie within the range of the over-voltage of the hydrogen or oxygen.

According to the new method, it is possible to undertake the development at the potential at which the development works free from fog and with large γ -values. Since the electrode potential of reversible oxidation-reduction systems often depends upon the pH value, as, for example, in the case of anthraquinone or indigo derivatives, it is advisable in such cases to maintain constant the actual hydrogen-ion concentration, which can be accomplished either by the addition of buffer systems, such as acetic acid-sodium acetate mixtures, borax-boric acid mixtures or, alternatively, by blowing-in of carbonic acid, adding drops of acid, or by means of neutralization anodes and the like. Such a mode of working is furthermore indicated particularly when the electrodes are not arranged in the developing vessel. When a diaphragm is used, the passage of current liberates hydroxyl ions of the water at the cathode and additions are necessary to maintain the pH value of the developer solutions. This maintenance of the reduction potential at a constant value, on the one hand, by the electrolytic influencing, and on the other, by the maintaining constant of the pH value, would not produce any suitable developer liquids within the ranges of the hydrogen or oxygen over-potential since, as experience shows, in these ranges, the potentials set in only badly or very slowly.

During the photographic development of halogen silver, halogen ions become free. Although the potential of the redox system is not influenced thereby, the effectiveness of the developer would nevertheless vary in the event of an enrichment of these ions in the developer. If it is desired therefore to maintain constant the effectiveness and also the γ -value with continuous or frequently repeated use of the developer, the halogen ions must be removed from the developer. This is possible in many ways: for instance, by the addition of thallium salts, forming thallos halides, the disturbing halogen ions

can be bound and removed. However, the halogen ion is discharged at the anode and the halogen atoms then may be organically bound by means of organic compounds, for instance, by means of phenol, orthocresol and the like.

It is also possible to make use, in this case, of the addition of so-called "catalyst" for halogenation, such as iodine, iron, tin and the like in the electrolyte, in order easily to bring about the desired substitutions.

The manner in which the electrical treatment of the developer liquid is carried out in detail is, in principle, immaterial for the mode of working. Only the electrode potential of the oxydation-reduction systems used as developers must be capable of being electrolytically influenced. Thus, for instance, the development may be carried out in such a manner that the developing vessel is formed as an electrolytic cell. However, it is also possible to work in such a manner that the developer is allowed to flow through the developing vessel and the developer is subjected on its way, outside the developing vessel, to the electrolytic treatment according to the invention, it being again possible to take the electrodes or even only one electrode out of the developing liquid and to use divided cells.

It is advantageous, with this mode of working, to use the developing fluid as catholyte, because then the anolyte, in which the halogen ions are concentrated by ionic migration, can easily be renewed or the oxidized halogen ion can easily be organically bound there.

The electrolytic reduction of the oxidation reduction systems for the purpose of development is not only performed directly, but can also take place through an intermediate body, namely, a catalyst of reversible or irreversible potential. Thus, for the purpose of development, a photographic silver halide layer is bathed during or after the electrolysis of a oxidation-reduction system, as, for example, indigo-carmin in the presence of sulphite or bodies which, like iron vanadium etc. salts, can easily alter their valency.

As has further been found, many oxidation-reduction systems necessitate, on the electrolytic reduction of a cathode, high or medium overpotential. They are then reduced, as, for example, rosinduline-G, at cathodes of thallium, lead peroxide or the like. Latent images can also be developed on silver iodine with reduced forms (that is, leuco compounds of the oxidation-reduction systems, which is of importance).

Practical examples

1. A developing vessel for film strips is filled with 100 litres of a 1% solution of β -anthraquinone sodium sulphonate, of which the pH value for the development of a negative emulsion preferably consisting of silver bromide is adjusted by buffering by means of acetic acid-sodium acetate within the range of pH4 to pH5. Immersed in the developing vessel are two carbon electrodes at a distance apart of 150 mms. With the quantity of conducting salt used as buffer in the example, a potential of 8 volts has proved to be suitable. Immediately after the application of the potential difference, the β -anthraquinone

sodium sulphonate is reduced in the vicinity of the cathode to the green anthrahydroquinone stage. The reduction is continued until a substantially equi-molecular mixture of the anthraquinone and anthrahydroquinone stages is obtained, the current density at the cathode being chosen so high for the purpose of obtaining a good current output, that no visible bubbles of hydrogen arise. This equimolecular condition can, for example, easily be determined colorimetrically and potentiometrically in known manner. The film strip is now introduced into the now finished developer and the current density is moderated to such an extent that the equimolecular ratio is substantially maintained throughout the development. The maintenance of the reduction potential can be carried out entirely automatically if there are used for the colorimetric control, photo-cells, which in turn control the electrolysing current. In this manner, many kilometres of picture or sound strips can be developed in the same developing bath, without a fluctuation occurring in the γ of the developed film.

2. A developing vessel of 100 litres capacity is charged with a 3% solution of o-cresol-indophenol, which has 5 gms. sodium carbonate in 100 ccs. solution. To the developing vessel, which is designed in the usual manner, there is connected a circulating system for the developer liquid, this system leading through an electrolytic cell which is constructed in such a manner that the developer solution is in the cathode compartment of the cell. In this cell there serves as catholyte a cold-saturated soda solution, which is separated from the catholyte by a steatite diaphragm of 3 mm. thickness. Symmetrically arranged on both sides of the diaphragm are electrode plates of stainless steel having a surface area of 250 sq. cms. on one side. After switching-in a voltage of 6 volts, the circulating developer liquid is reduced to the leuco stage, the blue colour of the electrolyte brightening considerably. The film strip to be developed, a silver bromide-containing negative emulsion, is now introduced into the developing trough, and the electrolysis in the electrolysing chamber is adjusted in accordance with the oxidation of the leuco stage.

In this practical example, the halogen ions which become free during development migrate from the developer into the anolyte. If phenol is added to the anolyte, until it contains about 1% phenol, tribromo-phenol is separated at the anode.

In the chosen practical example, blue dye, which is soluble in water, is separated near the silver. When choosing other indophenols and otherwise the same mode of working, it is possible to give a blue colour to the pictures on the picture strip; the silver can then be dissolved out with a known silver solvent, so that a blue organic picture remains behind.

This form of carrying out the method would also be suitable for the colour development for use in connection with colour photography, by treating in one or more emulsion layers in the above described manner.

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