PUBLISHED

MAY 4, 1943.

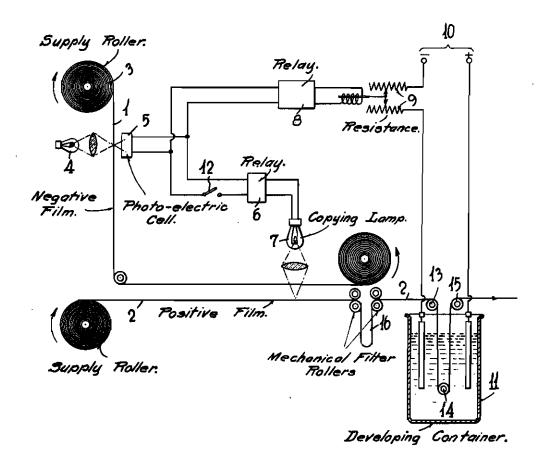
BY A. P. C.

J. RZYMKOWSKI

DEVELOPING PROCESS

Filed July 5, 1940

Serial No. 344,143



Johannes Azymkowski
Olivertor
What
Chickey Model

ALIEN PROPERTY CUSTODIAN

DEVELOPING PROCESS

Johannes Rzymkowski, Jena, Germany; vested in the Alien Property Custodian

Application filed July 5, 1940

The present invention relates to a process of developing photographic picture- and soundrecord copies in dependence on the density of and/or the contrasts in the negative. In carrying out the process according to the invention reversible developers, i. e. oxidation reduction systems, are used the reduction potential of which is adjusted according to the density of and the contrasts in the negative respectively. This matically be effected according to the invention in dependence on the density of and the contrasts in the negative respectively. The mode of operation is applicable with equal advantage for copying and developing respectively of individual pic- 15 tures and series pictures and particularly also of sound- and sound picture-strips.

During the production of picture strips in the film studio it cannot be prevented that in alternate succession outside and inside pictures and 20 scenes at night time, i. e. at the most different conditions of illumination and ranges of objects are to be shooted. After developing the negative, therefore, one and the same film reel shows negative portions of most various densities.

To ensure a good reproduction it is absolutely necessary to equalize these differences as far as possible in the positive film.

This first has been tried by ascertaining the density of the essential points of the picture from 30 solutions. one scene to another and then varying the light of the copying apparatus accordingly. This socalled "ascertaining of brightnesses," however. proved to be too time consuming in practice. Thereupon on a photo-electric basis the density 35 are anthroquinines besides anthrahydroquinones, of the negative has continuously been scanned and the currents of the photo-electric cell have been used to control by way of relays or the like the quality or the brightness of the light of the lamp in the copying apparatus.

This compensation method, however, is under no circumstances perfect, because the following development is carried out with constant developer intensity regardless of what has previously happened with the negative or positive.

Here the process claimed as new starts.

By replacing the hitherto used irreversible developers by reversible systems it is rendered possible to adjust the reduction potential of the dethe negative. In this manner the copy of a scene having large contrasts between light and shadow is tried to be equalized by a soft development, i. e. by a low reduction potential. Inversely it must by adjusting the reduction potential, if for instance scenes are to be copied which necessarily must be shooted at fog.

Preferably as hitherto in carrying out the above mentioned primitive method of "ascertaining of brightness" the density of and the contrasts in the negative are not manually determined and the addition of the reduction agent necessary for the adjustment of the reduction potential also is adjustment of the reduction potential may auto- 10 not regulated according to circumstances from the outside, but the two operations are coupled together. This mode of operation is of particular advantage in the electrolytic reduction of oxidation reduction systems. As is well known there are reversibly oxidizable developers and irreversibly oxidizable developers. The irreversibly oxidizable developers hitherto quite generally have been used in the technics. To these developers belong the well known developers, as metol, hydroquinone, pyrocatechin, rhodinal, glycine and so on. Samples of the reversibly oxidizable developers are the anthraquinones and anthrahydroquinones respectively which hitherto had not been used as developers. As in the case of 25 anthraquinones and anthrahydroquinones respectively oxidations and reductions respectively coupled with reversible operations are concerned, the oxidized as well as the reduced phase of the substance in question usually are present in the

This mixture of the oxidized and reduced phase is the reason for the formation of the potentials called oxidation-reduction-potentials. Such mixtures or oxidation-reduction systems for instance and indigo besides indigo white. Depending on the chemical nature of the substance and the proportion in which the oxidized and reduced phase of this substance are present the potential 40 assumes different values.

Samples of suitable oxidation reduction systems are for instance:

Anthraquinones, phenanthrenquinones, indophenols, aminoindophenols, indamines, thiacines, 45 oxacines, safranines, rosindulines and rosindones, viologenes, but also conjugated systems having open chains, as vitamine C, heterocyclene, as indigo derivatives, organic complexes of the type Alkx ((R.COO), Mez), as iron citrates and the veloper solution in dependence on the density of 50 like. These oxidation reduction systems represent a mixture of the oxidized and reduced forms the designation of the oxidation reduction systems always is effected according to the oxidation or O-form. In accordance with the invention be tried to enhance the contrasts in the positive 55 such an oxidation reduction system is used as

2 344,143

developer and the reduction potential desired at the time which, of course, may be different from case to case is electrolytically adjusted.

If for instance during development the reduction potential is to be maintained at a constant 5 value to obtain a constant reduction potential in the developed silver halide layer, the developer in each case is reduced in the degree in which it oxidizes.

For this mode of operation the use of reversible 10 systems as developer is of importance, because in this manner only equilibrium may permanently be maintained and influenced in any desired sense respectively. The usable oxidation reduction systems must be capable of being adsorbed 15 by the silver halide and nucleus respectively.

Oxidation reduction systems capable of adsorption are only such systems which either are adsorbed by the latent picture of the metal salt layer or the metal salt itself. If for instance a 20 silver halide layer, as silver bromide, is exposed to light it adsorbs for instance the oxidation reduction system: anthraquinone (anthrahydroquinone, whereas the oxidation reduction system ferri-pyrophosphate) ferro-pyrophosphate is not 25 adsorbed. If the first mentioned oxidation reduction system is subjected to electrolysis the latent image is developed in the silver halide layer, whereas a cathodic reduction as powerful as possible of the second mentioned system does 30 drawing may be provided as indicated by the innot result in the formation of any developer solution.

The present invention, however, is not limited to this mode of operation which is based upon the electrolytic reduction of oxidation reduction 35 systems, but may be used in the same manner in connection with any desired reduction of an oxidation reduction system, for instance by the aid of gaseous hydrogen or solid reduction agents which for instance may consist of silver or cad- 40 mium, the use of catalyzers some times being of advantage.

In the accompanying drawing one device for carrying out the process according to the invention is diagrammatically shown by way of $_{45}$ example.

The negative film I is to be copied upon the positive film 2. The negative film 1 is unwound from the supply roller 3 and passes along the source of light 4, whereby the oppositely arranged 50 photo-electric cell 5 is energized in accordance with the density of the film portion just situated between the source of light and the photo-electric cell. By way of a relay 6 the current coming from the photo-electric cell 5 may control the 55 brightness of the copying lamp 7. By way of a relay 8 and a resistance 9 this current may also be used to control the current of the electrolysis which is derived from the source of current 10. This current effects electric development in the 60 container 11 in which the positive film 2 slowly and continuously is passed over rollers 13, 14 and 15. The currents of the photo-electric cell 5 may be supplied as desired to the two relays 8 and 8, or, by the aid of the circuit breaker 12, the relays 65 8 and thereby the current serving for the development may be controlled. The operation is such that if the negative is rather flat a more intense current is used for the electrolysis, whereas for negative portions with large contrasts the current intensity is automatically reduced. The control of the reduction potential, however, may also be combined with the arrangement of the copying light 7. Instead of the device for effecting elec-

the oxidation reduction system may permanently be maintained by blowing gaseous hydrogen into the development vessel which is provided with one or more catalyzers. The relay 8 then does not operate a regulating resistance, but the reducing valve of a hydrogen bomb.

This automatic regulation of the current of electrolysis or of the reducing agent may advantageously be effected by control records the contrasts of which are arranged in dependence on the density of or the contrasts in the nega-

By lifting and lowering the rollers 13, 14 and 15 the film may remain in the electrolyt for a shorter or longer period of time respectively. As the reduction potential of the development vessel, controlled by the photo-electric cell, may, in dependence on the size of the system, operate eventually with a certain inertia, the way the film must perform from the point of copying to the development vessel must be chosen of such length that the reduction potential always is adjusted in the development vessel as soon as the corresponding scene is introduced into the development vessel. This is obtained by correspondingly choosing the length of way between the point of copying and the development vessel. Therefore, in the example illustrated in the drawing one or more film loops not shown in this terruption of the path of the film 2 at 16 between the point of copying I and the development vessel 11. Moreover, instead of a single electrolyzer several electrolyzers, united to an aggregate, may be provided each of which preferably has the form of a tube.

Since oxidation reduction systems are, as is well known, pH-sensible, it is possible to use the currents coming from the photo-electric cell 5 for influencing the pH-value, for instance in such a manner, that such currents control the valve by way of which acid is continuously supplied to the development vessel. In connection with some oxidation reduction systems it is advisable to use the photo-electric cell to simultaneously control the current of electrolysis, the copying light and the pH-value, whereby preferably current regulating resistances are arranged in the circuit of the three relays. In the drawing the regulation on the pH-value is not shown.

The other modes of operation for developing by means of oxidation reduction systems capable of adsorption the reduction potential of which is, during development, maintained or adjusted at times may, of course, all be used in connection with this mode of operation. The mode of operation, moreover, is not limited to the use of definite oxidation reduction systems and also not to the development of silver halide layers as other photographically usable metal silver halide layers, as for instance mercury halides, thallous halides, complex cobalt salts, etc., may be used in the same manner.

In the drawing the picture negative only has been indicated. In a corresponding manner the sound negatives also are copied and finally, by the use of a corresponding copying apparatus. the picture negative as well as the sound negative may be copied upon a common positive film. Special scanning members connected to photoelectric cells will be provided for the picture negative and for the sound negative respectively.

By this mode of operation it is possible to obtain the most suitable u-value of the sound strip trolysis shown in the example, the potential of 75 and of the picture in the developed positive film. 344,143 **3**

In particular the entire sound strip of the developed film roller is maintained constant in an excellent manner. Hereby the old drawback of sound fluctuations occurring when projecting films in cinemas is strongly opposed.

The new method may also be used in connection with color films by selectively adjusting to an optimum either the color development of the picture or the silver- and silver sulphide precipitate respectively of the sound strip. It is of no importance, whether the natural color picture is produced in one layer or in several superposed layers. A modification of this photoelectrically controlled color development consists in using in the development vessel oxidation reduction 15 systems the oxidation phases of which are insoluble and colored. Hereby the developed layers themselves are colored so that monochromatic or polychromatic pictures are obtained from which the silver or the insoluble coloring substance may 20

selectively be removed. In any case always oxidation reduction systems are concerned, as are for instance quinones, anthraquinones, phenanthrenquinones, indigo derivatives, thiazines, oxazines azines, safranines, viologenes, rosindulines, indamines, indophenols, aminoindophenols, or these oxidation reduction systems as indophenols, aminoindophenols, indamines respectively are electrosynthetically to be produced from preliminary products not developed, this production eventually being carried out in the development vessel. The coupling components necessary to obtain this production may be present either in one layer or in a plurality of layers of the metal salt layers of the film, i. e. in the film itself or else in the development vessel itself.

The precipitation of the foreign ions, for instance halogen ions, is chemically or electrochemically effected in the usual manner.

JOHANNES RZYMKOWSKI