Patented Feb. 19, 1924. 1,484,029

UNITED STATES PATENT OFFICE.

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MULTIPLE-STEP PROCESS OF PHOTOGRAPHIC REPRODUCTION.

No Drawing. Application filed October 7, 1919. Serial No. 329,078.

To all whom it may concern:

Be it known that I, ROBERT JOHN, a citizen of the United States, residing at New York, in the county of New York and State of New York, have invented a certain new and useful Multiple-Step Process of Photographic Reproduction, of which the following is a specification.

My invention relates to a multiple step process of photographic reproduction and has for its object to produce a printing surface containing a photographic record of lights and shades from which copies can be made by a dye or ink contact transfer process. An illustrative dye contact transfer process is disclosed in patent to Shepherd and Bartlett, No. 728,310, granted May 19, 1903, for photographic printing, and an illustrative ink contact transfer process is disclosed in Cassell's Cyclopaedia of Photography, Cassell & Co., New York, 1912, at page 124, under the title "Collotype," it being understood, however, that the processes thus illustrated do not use a printing plate having the novel and beneficial characteristics of the printing plate disclosed herein. Although the preferred method is to obtain the photographic record for the printing surface from a completed negative, it may be obtained by direct exposure, as, for example, in a camera, the details of which method are disclosed in a copending application for Letters Patent Serial No. 327,890, filed October 2, 1919, for process of photographic reproduction directly from a negative. The printing surface when treated with dye or ink also may be used in the same manner as a positive, either for direct view, or with reflected light, or with transmitted light as in a projecting machine.

The invention is applicable to monochromatic, polychromatic, or natural color photography both in still photography and in motion picture photography. The term "color" is intended to include "black," which sometimes technically is designated as an absence of color.

In the embodiment of my invention chosen for purposes of illustration, a sensitized emulsion such as a silver salt emulsion is exposed to the action of light modified by the lights and shades of the completed negative which it is desired to reproduce. The silver salt emulsion may be carried or mounted on any desired support, either opaque, translucent, or transparent, but preferably is mounted on a transparent carrier such, for example, as glass or a cellulose base, in order that the silver salt emulsion may be exposed to the modified light through its transparent carrier.

The emulsion then is treated by a developing and hardening process comprising a plurality of steps so that the emulsion can be examined at an intermediate stage or stages and the remaining step or steps adapted to produce with great certainty the desired result. The process is adapted to render insoluble or unremovable the emulsion adjacent its light-affected, light-sensitive content, after which the soluble unhardened or removable portions of emulsion are removed in any desired manner, as for example, by melting with warm water.

The result of the above treatment is the production of what may be termed a printing surface having novel characteristics and beneficial properties never before attained.

The most important of the novel characteristics is a printing or reproducing surface comprising granules or great numbers of photographically formed, extremely minute, individual protuberances which are distributed and grouped irregularly so as to represent photographic lights and shades.

The most important of the beneficial properties is that such a printing surface when treated with a dye, ink, or other coloring matter, will absorb or take up or carry the coloring matter within a few seconds, and when thus treated and placed in contact with a substance which is to carry the final reproduction such for example as a gelatin, will give up its coloring matter practically instantaneously and produce on said gelatin an exact and perfect reproduction. This speedy result, which is novel and was impossible of attainment before the present invention, is of prime importance in the production of motion picture positives from motion picture negatives, although the saving of time and the superior results obtainable in still photography also are important. The printing plate or film, moreover, when treated with coloring matter, may be used as a positive if reproductions are not desired.

For purposes of illustration, a two step process will be described, the first of which changes the light-affected sensitized par-

ticles to metallic silver and partially hardens the emulsion adjacent each particle, and the second of which completes the hardening of said adjacent emulsion.

The first step of the embodiment chosen for purposes of illustration, comprises treating the exposed emulsion with a developing solution containing a hardening or tanning agent which partially renders insoluble or unremovable the emulsion adjacent its light-affected, light-sensitive content, the effect of which agent is controlled or limited selectively by the presence of varying quantities of a neutralizing agent.

A sample formula for a developing solution containing a hardening or tanning agent the effect of which is controlled and limited selectively by the presence of varying quantities of a neutralizing agent is as follows:

Water, 8.5 ounces.
Pyrogallic acid, 11 grains.
Metol (monomethylparamidophenol sulphate), 9 grains.
Potassium bromide, 4 grains.
Sodium carbonate, 200 grains.
Sodium sulphite substantially over 60 to 80 grains.

In the above sample formula the hardening or tanning agent is pyrogallic acid, and the controlling and limiting agent is sodium sulphite which may be varied in amount selectively within limits to obtain the desired result. It is well known that pyrogallic acid also is a developing agent and that sodium sulphite is a preservative adapted to prevent oxidation of the pyrogallic acid in solution. Other hardening and tanning agents and other neutralizing agents may be used, the above formula representing one developing solution by which the process may be carried out. The main difference between the above sample formula and standard developing formulas is in the amount of sodium sulphite used. In standard formulas the amount of sodium sulphite used is so greatly in excess of the amount used in the above sample formula that the tanning or hardening effect of the pyrogallic acid is entirely neutralized or overcome. In the sample formula, the sodium sulphite merely controls and limits the hardening effect of the pyrogallol. It is of course understood by those skilled in the art that when a thick layer of emulsion is treated, or when the exposure is through the transparent carrier, it is advisable, in order to accelerate the action of the pyrogallic acid, to use larger quantities of an accelerator such, for example, as sodium carbonate or its equivalents than when the emulsion layer is thin or exposed on its face. When larger quantities of sodium carbonate thus are used, it is necessary to increase the amount of sodium sulphite. The above sample formula is for treatment of an emulsion exposed through its transparent carrier and therefore contains a comparatively large amount of sodium carbonate with an increased amount of sodium sulphite. In order to obtain the desired partial hardening, however, the amount of sodium sulphite in the process disclosed herein is much less than would be used in a developing solution for the usual development of the particular emulsion layer to be treated. Although it is preferable for reasons of convenience to embody the selectively controlled hardening agent in the developer solution, it may be used separately if desired, by such modification of the developer solution as will prevent such a hardening of the emulsion as will prevent the selective hardening desired.

It is believed that the hardening or tanning effect of the pyrogallic acid exerts its action first adjacent the so-called latent image, or in other words, on the portions of emulsion adjacent the particles of silver salts affected by the exposure light and converted by the developer into metallic silver. Thus in a silver bromide film, the throwing off of the bromide from a light-affected silver bromide particle in the developing process, probably reacts with the pyrogallic acid to harden or tan or render insoluble or unremovable the adjacent emulsion. Thus in the embodiment chosen for purposes of illustration, the reaction products from the chemical effects of the developer solution, are believed to react with the selectively controlled hardening agent. The essential result is a partially hardened emulsion surface corresponding to the lights and shades to be reproduced. By controlling the hardening or tanning effect of the pyrogallic acid as above set forth, only the particles of emulsion adjacent the said light-affected particles of silver salts are hardened, the relative proportions of the hardening agent (whether or not accelerated by an accelerating agent) and of the neutralizing agent being such as to control selectively the effective area of influence of the hardening agent. It is preferable that only those portions of emulsion be hardened which are adjacent the carrier for the emulsion, which may be accomplished in various ways, some of which are disclosed in my copending applications for Letters Patent Serial No. 313,239, filed July 25, 1919, for a thin mounted sensitized emulsion; Serial No. 313,240, filed July 25, 1919, for process of making a contact transfer printing surface by complementary light; Serial No. 327,891, filed October 2, 1919, for potassium iodide formula for photographic processes, process of using same, and article obtained thereby; and in my Patent No. 1,453,258, dated April 24, 1923, for process of making a contact transfer printing sur-

face with a colored emulsion, and among which may be mentioned the exposure of the sensitized emulsion through its transparent carrier and the limitation of the depth to which the rays of exposure light penetrate by having the actinic rays of the exposure light and the emulsion complementary in color.

The partially hardened emulsion preferably then is fixed to remove the unreduced silver salts.

As the sensitized content of the partially hardened emulsion has been changed to metallic silver by the action of the developing solution, the complete hardening of the emulsion can be accomplished by treatment with a hardening solution which reacts with metallic silver. As the emulsion can be examined at this intermediate stage of hardening it is possible to vary the process of complete hardening to obtain with great certainty any desired printing surfaces.

The second step of the embodiment chosen for purposes of illustration, comprises treating the partially hardened emulsion with a solution containing an agent which renders completely insoluble or unremovable the emulsion adjacent its metallic silver content, the effect of which agent is controlled or limited selectively by the presence of varying quantities of a neutralizing agent, after which the soluble or removable portions of emulsion are removed in any desired manner, as, for example, by melting with warm water.

A sample formula for a treating solution containing a hardening or tanning agent the effect of which is controlled and limited selectively by the presence of varying quantities of a neutralizing agent is as follows:

Water, 20 ounces.
Potassium bichromate, 1024 grains.
Sulphuric acid, 3 to 4 ounces.
Water, to 32 ounces.

Add four (4) ounces of above solution to twenty-eight (28) ounces of water. Use half and half with water.

In the above sample formula the hardening or tanning agent is potassium bichromate, and the controlling and limiting agent is sulphuric acid which may be varied in amount selectively within limits to obtain the desired result. Other hardening and tanning agents and other neutralizing agents may be used, the above formula representing one treating solution by which the process may be carried out. Hydrochloric acid, for example, as well as other acids may be used, the above formula representing one treating solution by which the process may be carried out. The tanning or hardening effect of potassium bichromate on the emulsion surrounding a metallic silver was known previous to my invention, but the method of controlling the tanning or hardening effect so that a too contrasting or paddy relief was obviated and the desired granular printing surface obtained was not known previous to my invention. Thus if potassium bichromate without any sulphuric acid or with only a very little sulphuric acid is used to treat metallic silver in an emulsion, the tanning or hardening action is so great that a too contrasting or paddy relief is obtained. As more acid is added, however, the relief becomes thinner until the point is reached where the amount of acid added produces a relief characterized by the granular printing surface desired. If acid is added beyond this point, the tanning or hardening effect of the potassium bichromate will be neutralized entirely so that all the emulsion would dissolve from the carrier when treated with warm water.

It is believed that the hardening or tanning effect of the potassium bichromate exerts its action first adjacent the particles of metallic silver. The potassium bichromate probably reacts with the metallic silver to throw off products of reaction which harden or tan or render insoluble or unremovable the adjacent emulsion. The essential result is a hardened emulsion surface corresponding to the lights and shades to be reproduced which will acquire and give up any desired color in a comparatively short time. By controlling the hardening or tanning effect of the potassium bichromate as above set forth, only the particles of emulsion adjacent the said metallic silver are hardened. The unhardened portions, as stated above, then may be removed in any desired manner as by placing the emulsion in warm water which causes the unhardened or soluble portions to soften and melt away from the hardened or insoluble portions so that the hardened emulsion alone will remain in the form of extremely minute, individual protuberances which are distributed and grouped irregularly so as to represent the photographic lights and shades which it is desired to reproduce. It is preferable that only those portions of emulsion be hardened which are adjacent the carrier for the emulsion, which may be accomplished in various ways, some of which are disclosed in my Patents, Nos. 1,374,853, dated April 12, 1921 and 1,417,328, dated May 23, 1922 in my copending applications for Letters Patent Serial Nos. 327,889, filed October 2, 1919, 327,890, filed October 2, 1919, 313,239, filed July 25, 1919 and 313,240, filed July 25, 1919, and among which may be mentioned the exposure of the sensitized emulsion through its transparent carrier and the limitation of the depth to which the rays of exposure light penetrate by having the actinic rays of the exposure light and the emulsion complementary in color.

Although the treating solution referred

to acts also as a bleach, the hardened emulsion may be bleached further if desired to remove any black metallic silver not already bleached. This may be done in well known manner, and while not necessary, is of advantage as it enables the operator to watch the effect of the coloring matter on the printing surface to which it is applied for carrying out the printing process.

The order of melting, bleaching, and fixing is not important and may be carried out in any order desired, although it generally is more convenient to fix, bleach, and melt, in the order named.

The printing of positives from the printing surface may be done by direct contact. The printing surface is exposed to the action of the desired coloring matter as by placing it in or carrying it through a liquor color bath. The colored surface then is placed in contact, preferably under some pressure, with the substance on which the positive is to be made, as by a roller or by a squeegee. As stated above, the printing surface prepared by my process receives and gives up the coloring matter almost instantly as distinguished from other processes which take an appreciable length of time.

Natural color effects may be produced in well known manner, such for example as by exposure through color screens with subsequent treatment and manipulation to obtain the desired results.

Many modifications of my invention will be apparent to those skilled in the art without departing therefrom or from the scope of the claims, my invention not being limited to the embodiments thereof chosen for purposes of illustration but consisting of a process for forming a printing surface capable of acquiring and giving up a desired color with great rapidity by treating an emulsion by a multiple step process which hardens the emulsion to correspond to the lights and shades desired to be reproduced.

Having described one embodiment of my invention, what I claim is:

1. The process of forming a photographic record of lights and shades capable of use as a transfer printing plate, which comprises developing an exposed photographic emulsion with a partial-emulsion-hardening solution and then hardening portions of emulsion adjacent the light affected sensitive content of the emulsion with an agent adapted to harden said emulsion by reaction with the light affected sensitive content of the emulsion, and with a neutralizing agent for said hardening agent, the relative proportions of said hardening and neutralizing agents being such as to control selectively the effective area of influence of the hardening agent but to an extent less than the complete neutralization of said hardening agent.

2. The process specified in claim 1 in which the hardening agent is potassium bichromate.

3. The process specified in claim 1 in which the neutralizing agent is sulphuric acid.

4. The process specified in claim 1 in which the hardening agent is potassium bichromate and the neutralizing agent is sulphuric acid.

In testimony that I claim the foregoing, I have hereunto set my hand this 2nd day of October, 1919.

ROBERT JOHN.