UNITED STATES PATENT OFFICE.

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PROCESS OF PRODUCING COLORED IMAGES.

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To all whom it may concern:

Be it known that I, EDMUND R. BULLOCK, residing in Rochester, county of Monroe, State of New York, have invented new and useful Improvements in Processes of Producing Colored Images, of which the following is a specification.

This invention relates to photography and more particularly it relates to the production of colored images. In my process I obtain, preferably from a primary photographic image of the silver species, an intermediate image containing chemically active substances and treat it with suitable compounds which, upon reacting with said image, produce insoluble colored substances or dyes, the result being a colored image having the same general size and gradations as the primary image. Such image may then be fixed.

One object of my invention is to provide a process of this kind which will easily yield images of clear, brilliant, durable, readily reproducible, and definite colors on paper, glass, film, or other base. Another object of my invention is to form an intermediate image of metallic insoluble salts of such a nature and of such a state of high oxidation that they will have strong oxidizing tendencies toward the organic compounds with which they react to form the colored image; yet will themselves be not reduced to the metal but merely to a salt, which is in a low state of oxidation and is easily removable by a fixing bath. In other words I aim to carry on the color forming reaction on what may be termed a relatively high plane of oxidation, none of the reaction products being reduced to the lowest limit, the words "oxidation" and "reduction" being used herein with the broadest chemical significance to refer to chemical bonds and changes therein generally, and not merely to oxygen content. A third object of my invention is to provide a bleaching bath or step which will act rapidly to produce this intermediate or secondary image, yet will not cause injury to such image or its support, if the bath be used for a prolonged time. A fourth object is to provide a process which may be carried out by using relatively inexpensive baths of good keeping qualities. A fifth object of my invention is to employ in the fixing operation a bath which will quickly dissolve metallic salts but will not appreciably reduce or injure the insoluble colored image. A sixth object of my invention is to provide auxiliary clearing and washing steps where necessary. Other objects will hereinafter appear.

To enable those skilled in the art to use my invention, I shall now describe certain specific embodiments thereof but it is understood that these particular embodiments are merely illustrative and the scope of the invention is not limited to these described examples except as indicated in the claims.

As one example of my process I will explain its application to the production of colored images on paper starting with the usual image composed of minute silver particles suspended in any ordinary colloid, such as gelatin or collodion. The silver image is immersed in a bleaching bath made up of 4 parts of a 10% potassium ferricyanid solution and 1 part of a 1% potassium permanganate solution. The image is changed to a uniform yellow or orange color and the end point of the action is recognized thereby. The treatment is usually about a minute in length but a much longer immersion is found to be not detrimental. This bleaching bath can be used repeatedly, but in the case of an old bath it is often advisable to filter it and then add about one-tenth of its volume of potassium permanganate solution. This is to keep the bath in a sufficiently oxidizing condition to prevent the formation of silver ferrocyanid, which salt is useless at this stage of the process, the yellow silver ferricyanid with its high state of oxidation being the salt desired.

When the bleaching is complete, the image or print is removed from the bleaching bath and washed in running water. The first washing may vary according to the support for the image and usually will not exceed thirty minutes.

The print containing the intermediate image of practically insoluble silver ferricyanid at this state of the process will often show brownish stains, probably due to manganous ferricyanid. These may be removed by immersion for 5 to 10 minutes in

a bath containing 5% of oxalic acid crystals. The print should be left in the clearing bath some time after the disappearance of the brownish stains to entirely remove the undesirable salts. Should white manganous ferrocyanid separate from a used oxalic acid bath it should be removed before the bath is again used or a fresh bath should be prepared. After the clearing operation, the print is again washed, say 20 minutes, in running water and the secondary image of silver ferricyanid will then be complete and may be either dried and kept for a subsequent toning or transferred at once to the toning bath.

Alternatively the silver ferricyanid image may be formed by bleaching the silver image in a bath composed of 5 parts of a 10% potassium ferricyanid solution and 2 parts of a 10% chromic anhydrid (CrO_3) solution. This bath acts fairly quickly, 2 minutes being a common time for bleaching. A clearing bath is not needed after it but a long washing is sometimes necessary and may last for two hours in running water. In use this alternative bath may require a little practice in manipulation.

Whichever bleaching bath is used, it should be free from more than traces of chlorids. The wash water should also be reasonably free from them because the chlorids might change some of the silver ferricyanid to silver chlorid thus weakening the oxidizing power of the intermediate image.

The toning bath in which the ferricyanid image is next immersed is a solution containing organic substances which are capable of being oxidized by the action of silver ferricyanid into insoluble colored substances. As examples of such substances I may name (1) benzidin which gives a strong blue image; (2) O-tolidin which gives a strong green image; (3) paramidophenol together with alpha-naphthol which give a red image; (4) paraphenylenediamin which gives a purplish image; (5) alpha-naphthylamin which gives a reddish-purple; (6) dianisidin hydrochlorid which gives a strong green image. These illustrations will serve to show the kind of materials which can be used in my process. The strength of the toning bath is not especially important, even fairly dilute baths giving a rapid action which is often complete at the end of a minute.

The theory (which is, of course, not indispensable to practising my process) is that these organic compounds act as reducers which change the silver ferricyanid of the secondary image into silver ferrocyanid and are themselves oxidized to colored substances which are insoluble and are formed or deposited in such a way as to create a colored image having the same general form, size, and gradation as the original or primary silver image. By thus keeping the reaction on a high plane of oxidation I am able to take advantage of the greater chemical activity in the formation of colored substances possessed by highly oxidized salts, such as ferricyanids, while obtaining at the end of the reaction a salt of lower oxidation which is more easily removed without injury to the colored image, than would be the case if the reaction had been on a lower level of oxidation and a metallic precipitate, like silver, had been produced.

The toned print is washed, say for five minutes, in running water to remove the excess of the toning bath. For some purposes the compound image of silver ferrocyanid and insoluble coloring matter may be satisfactory and sufficient.

It is often desirable, however, to eliminate the silver salts without injuring or disturbing the coloring matter, thus enhancing the transparency of the colored image. Due to the fact that the toning reaction has been on a relatively high plane of oxidation, thus resulting in silver ferrocyanid instead of metallic silver, this removal of the silver salt can be easily effected. If the original bleaching bath was the one containing potassium permanganate, the colored image is treated a short time, say 1 minute, in a bath containing sodium thiosulfate crystals 35 parts, potassium chromate 1 part, and water to 100 parts. The proportions of this bath are, of course, variable, but I have found the ones given to be very efficient. Such a bath is mildly alkaline and so stable that it can be boiled. The chromate checks any tendency to reduce the colored image. However, where the original bleaching bath contained the chromic anhydrid, this tendency toward reduction in the fixing bath does not prevail and a plain sodium thiosulfate fixing bath may be employed.

The fixed image or print is now washed for a time, sufficient to remove soluble crystalline salts therefrom.

In another species of my invention I may obtain an image of silver ferricyanid as hereinabove explained and then treat the same with a solution of manganous bromid, whereby a mixed image of silver bromid and manganous ferricyanid is formed. This image (after washing) is treated or toned with organic substances, such as benzidin and benzidin derivatives, to give colored images, the organic reducer being oxidized to produce an insoluble colored substance, and the manganous ferricyanid being reduced to manganous ferrocyanid. If desired, the silver bromid may be dissolved out before the toning bath is used by bathing in a 3% solution of potassium cyanid, such

operation leaving the manganous ferricyanid unimpaired. Experiments with silver bromid alone show that such substance does not react on the benzidin, etc., to produce a color and, consequently, the active re-agent in the mixed image is the manganous ferricyanid.

I claim:

1. The process of producing colored images which comprises forming an image composed of metallic salt in a high state of oxidation and reducing said salt to a metallic salt of a lower state of oxidation by treating said image with an organic reducing compound which is simultaneously oxidized to produce an insoluble colored compound forming a colored image.

2. The process of producing a colored image which comprises forming an image of an insoluble ferricyanid, and reducing it to the corresponding ferrocyanid by treating it with an organic compound which is simultaneously oxidized to produce an insoluble colored substance forming a colored image.

3. The process of producing colored images which comprises forming an image of silver ferricyanid and reducing it to silver ferrocyanid by treating said image with an organic compound which is simultaneously oxidized to produce an insoluble colored compound forming a colored image.

4. The process of producing a colored image from a primary image which comprises converting said primary image into an intermediate image containing a salt in a high state of oxidation, and reducing said salt to a salt of a lower state of oxidation by treating said intermediate image with an organic reducing compound which is simultaneously oxidized to produce an insoluble colored substance forming a colored image.

5. The process of producing a colored image from a silver image which comprises converting said silver image into an intermediate image of silver ferricyanid and reducing said silver ferricyanid to silver ferrocyanid by treating said silver ferricyanid with an organic reducing compound which is simultaneously oxidized to produce an insoluble colored substance forming a colored image.

6. In the process of producing a colored image from a silver image the step which comprises treating said image in a bath of potassium ferricyanid and potassium permanganate until a yellowish secondary image is obtained.

7. In the process of producing colored images from silver images the step which comprises treating the silver image in a bath containing 4 parts of 10% potassium ferricyanid and 1 part of 1% potassium permanganate.

8. The process of producing a colored image from a silver image which comprises converting said silver image into an image of silver ferricyanid, reducing said silver ferricyanid to silver ferrocyanid by treating said ferricyanid with an organic reducing compound which is simultaneously oxidized to produce a colored insoluble substance giving a colored image and finally dissolving out the silver ferrocyanid while leaving the colored insoluble substance intact.

9. The process of producing a colored image from a silver image which comprises converting said silver image into an intermediate image of silver ferricyanid, reducing said intermediate image to silver ferrocyanid by treating it with an organic reducing compound which is simultaneously oxidized to produce an insoluble substance forming a colored image, and finally fixing said colored image in a mildly alkaline bath containing a solvent of silver ferrocyanid together with a small percentage of an oxidizing agent.

10. In the process of producing a colored image, the step of treating an image containing a silver salt and insoluble colored substance in a bath containing sodium thiosulfate and a relatively small amount of potassium chromate.

11. In the process of producing a colored image, the step of treating an image containing a silver salt and an insoluble colored substance in an aqueous bath containing 35% of sodium thiosulfate crystals and 1% potassium chromate.

12. The process of producing a colored image from a silver image which comprises converting said silver image into a intermediate image of silver ferricyanid, washing the latter, treating the intermediate image in a clearing bath, again washing said intermediate image, and reducing said intermediate image by treating the same with an organic reducing compound which is simultaneously oxidized to produce an insoluble colored substance forming a colored image.

13. In the process of producing colored images, the steps of converting a silver image into a silver ferricyanid image by treatment in a bath containing potassium ferricyanid and potassium permanganate, washing the secondary image thus obtained, treating said secondary image in a bath of oxalic acid until the image is cleared from stain, and washing said image to produce a yellowish image of silver ferricyanid free from stain and soluble salts.

14. The process of producing a colored image from a silver image which comprises converting said silver image into an intermediate image of silver ferricyanid by treatment in a bath containing potassium ferricyanid and potassium permanganate, washing, treating said intermediate image in a

clearing bath containing oxalic acid, washing said intermediate image, reducing said secondary image by treating it with an organic reducing compound which is simultaneously oxidized to produce an insoluble colored substance forming a colored image, washing, fixing, and finally washing.

15. The process of producing a colored image from a silver image, which comprises converting said silver image into an intermediate image of silver ferricyanid by treating it in a bath containing potassium ferricyanid and potassium permanganate, washing, clearing in a bath of oxalic acid, washing, reducing in a bath of benzidin hydrochlorid, washing, fixing in the bath containing sodium thiosulfate and a small quantity of an oxidizing agent, and finally washing.

In testimony whereof, I have signed this specification in the presence of two witnesses this 2nd day of March, 1917.

E. R. BULLOCK.

Witnesses:
I. A. SCHMITT,
R. L. STINCHFIELD.