

# UNITED STATES PATENT OFFICE.

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## REPRODUCING PICTURES OR THE LIKE.

SPECIFICATION forming part of Letters Patent No. 770,533, dated September 20, 1904.

Application filed May 27, 1902. Serial No. 109,196. (No specimens.)

*To all whom it may concern:*

Be it known that we, WILHELM OSTWALD, doctor of philosophy and professor, and OSCAR GROS, doctor of philosophy, both subjects of the German Emperor, and residents of Leipzig, in the Kingdom of Saxony, German Empire, have invented new and useful Improvements in Reproducing Pictures or the Like, of which the following is a full, clear, and exact specification.

Our invention relates to a process depending upon reproduction by means of catalytic action. By "catalytic action" we understand the modifications in the rapidity with which chemical processes proceed, these modifications being produced by substances that do not exist among the substances produced by the chemical process. However, these substances may during the process participate in this process in any form—for instance, by intermediate reactions—and may undergo secondary changes—such as deposit of substances on the catalyzing surface, action on the reaction products, and the like. Another criterion of these catalyzing substances is that they are in no stoichiometric relation to the reagents and reaction products. Now there are numerous substances possessing these properties. Such substances are, for instance, metals such as platinum and silver, metallic salts, compounds containing or forming hydrogen ions, compounds containing or forming hydroxyl ions, oxids. In applying the catalytic properties of these substances in the reproduction of pictures we proceed as follows: We form first a picture or the like of the catalyzing substance. For example, a so-called "platinum print" produced by the ordinary photographic method may be used. Likewise silver prints—for instance, the so-called "salt-papers"—may be used. Other than photochemical means may also be used for the production of the original picture or the like which is to act as a catalyzing agent. For example, a drawing may be made with a saturated solution of potassium platinum chlorid and this transformed into a drawing in metallic platinum by means of a saturated solution of potassium ferrous oxalate. Also paper may be covered with a layer of man-

ganese oxid compounds by treating it with a weakly alkaline concentrated solution of potassium permanganate by means of a brush. This solution may be produced, for instance, by adding one gram of carbonate of soda to one hundred cubic centimeters of saturated potassium permanganate solution. By drawing on this paper, after washing and drying with a saturated oxalic-acid solution, after washing a drawing is produced in white lines on brown ground, which ground acts catalytically, while the lines do not. These original pictures we then use either for reproduction on paper or other carriers of the images or for producing the mechanical, physical, or chemical changes of metallic or other surfaces necessary for the production of printing-plates, and both these processes may be carried out directly or indirectly. The direct processes are based on the immediate action of the catalyzing substances upon a reaction mixture with which the paper or plate receiving the reproduction is covered, while in the indirect processes we produce or destroy in certain points of the original, by means of the catalyzing action, a substance which then reacts with other substances.

The following examples will illustrate our process.

### *Reproduction on Paper or the Like.*

*Direct process.*—Paper covered with a layer of substances whose reaction is accelerated by platinum is pressed close against the platinum print or other original drawing containing the catalyzing substance, whereupon reaction occurs much more quickly in the parts of the sensitive paper which are in contact with the platinum than in other parts. When the substances formed by the reaction are coloring-matters or colors or substances which by a suitable treatment may be transformed into coloring-matters or colors, or when such coloring-matters or colors or substances which may be transformed into coloring-matters or colors are decomposed by the reaction, a colored print corresponding in all details with the picture of the platinum print is produced.

Example 1: Paper is impregnated with a solution containing from one to five per cent. of

potassium bromate and from five to twenty-five per cent. of pyrogallol. When this paper is pressed on the platinum original, there is formed by chemical action in the parts in contact with the platinum a product which is a red coloring-matter and by means of metallic salts may be transformed into other colored substances. For instance, ferric sulfate, according to its concentration, transforms the red color into reddish brown to blackish gray. In this example other reactions of various kinds which are influenced by catalysis may be substituted for that between potassium bromate and pyrogallol. Such reactions are, for instance, those between potassium bromate and pyrocatechol, (by subsequent treatment with ferric sulfate blackish-blue pictures being produced,) potassium bromate and gallic acid, potassium chlorate and pyrogallol, potassium nitrate and pyrogallol, hydrogen peroxid and pyrogallol, hydrogen peroxid and pyrocatechol, hydrogen peroxid and gallic acid, hydrogen peroxid and anilin hydrochlorid, or the like.

Example 2: Against a silver-bromid gelatin plate or a silver-bromid paper which was exposed to the action of light for a moment we press a platinum print impregnated with a saturated solution of potassium bromate. Then in the parts where platinum exists the action of light is neutralized, and a silver print is obtained by developing in the usual manner.

*Indirect process.*—For indirect reproduction by means of catalysis the originals containing the catalyzing substance are treated with a solution of substances which at the parts of the original containing the catalyzing substance are more or less modified, accordingly to the quantity of catalyzing substance existing in every part. The original thus treated is then pressed either against paper or the like impregnated with substances upon which the modified substance can act or against ordinary paper and the like, the invisible image first produced then being developed by means of substances upon which the modified substances can act.

Example 3: We pour a solution of hydrogen peroxid over a platinum print. For instance, an ethereal solution may be used which is obtained by agitating an aqueous solution of hydrogen peroxid of thirty-three-per-cent. strength with twice its volume of ether and drying the ethereal solution by cooling down to 20° centigrade. At the parts containing platinum the hydrogen peroxid is destroyed by catalytic action with a speed which is a function of the quantity of platinum existing at every part of the original. The platinum print treated with hydrogen peroxid, as above set forth, is then pressed, after volatilization of the ether, for ten to forty seconds against a paper impregnated with a saturated solution of ammonium ferrous sulfate. The ferrous salt is then ox-

dized to ferric salt at the parts where there was no platinum, and the image can then be developed by various means—for instance, by means of potassium ferrocyanid or gallic acid, tannin, pyrogallol, pyrocatechol, or the like, of one-half to one per cent. strength, for instance.

Example 4: The platinum print treated with hydrogen peroxid is pressed against paper impregnated with a solution of a bichromate of five-per-cent. strength. An instable violet-brown image is thus formed, which by treatment with a solution of potassium permanganate of one-per-cent. strength is transformed into a stable one consisting of manganese oxids.

Example 5: If the platinum print treated with hydrogen peroxid is pressed against paper, an invisible print of hydrogen peroxid is obtained. If this invisible print is treated with a solution of a manganese salt—for instance, of fifty parts of manganese sulfate in one hundred parts of water, containing or not a small excess of ammonia—a visible picture formed of manganese oxids is produced. This picture is a positive one if the platinum print was negative.

Example 6: If in the foregoing example a saturated solution of ammonium ferrous sulfate is substituted for the manganese-salt solution and the print then treated with a pyrogallol solution of about one-per-cent. strength, a black print is obtained. Likewise other reactions influenced by hydrogen peroxid may be used.

Example 7: If the platinum print treated with hydrogen peroxid, as above set forth, is pressed upon so-called "rubber" printing-paper or "pigment" printing-paper and this then treated with a saturated solution of ammonium ferrous sulfate, the rubber or gelatin is tanned at the parts where the hydrogen peroxid was not destroyed and becomes more or less insoluble, accordingly to the concentration of the peroxid. The prints may then be developed in the usual manner.

In these indirect processes manganese-oxid originals produced, as above set forth, can be substituted for the platinum prints. In these examples various materials other than paper may be used as carriers of the sensitive substances—as, for example, gelatin and the like. In the direct process sticking of such a gelatin film to the picture which is to be reproduced must be prevented by first tanning the gelatin. Other catalyzing agents may also be added to the sensitive substances, such agents acting alone only very slowly, but in conjunction with platinum and other catalyzing substances much more rapidly. This combination of different catalyzing agents may also be effected by impregnating, for instance, the platinum original with a solution of these slowly-acting agents.

Example 8: Copper sulfate may be used.

Its concentration may vary in both cases and depends upon the time to be occupied in producing the picture. Even a solution of one-fifth-per-cent. strength may be used.

#### 5 *Production of Printing-Plates.*

*Direct process.*—For etching metallic plates we use substances which at the places in contact with the catalyzing substance produce a chemical action etching the metallic surface.

10 Example 9: We impregnate a platinum print with a saturated solution of potassium chlorate in acetic acid of from ten to fifty per cent. strength and press it upon a polished copper plate. The copper is dissolved from the parts in contact with the platinum of the original.

20 *Indirect process.*—An original containing the catalyzing substance is treated, as above set forth, with a substance which is modified by the catalytic action and then caused to act upon the surface of the plate to be used for printing purposes.

25 Example 10: A platinum print treated with hydrogen peroxid, as set forth in Example 3, is pressed against a plate covered with a layer of gelatin. If this plate is then put into a concentrated solution of ammonium ferrous sulfate, the gelatin is tanned at the parts where ferric salt is formed by the action of hydrogen peroxid and a rilievo is obtained which can be used for printing with fatty colors, the tanned parts only retaining these colors. Likewise

metallic plates may be etched indirectly. The metallic plate is then covered by means of the catalytic action with a coating of a substance which is either not attacked by acids or is not a conductor of electricity. The plate is then etched, either chemically or by means of a galvanic current.

40 Example 11: A platinum print treated with hydrogen peroxid, as set forth in Example 3, is pressed against a metal plate covered with a layer of fish-glue containing a chromate. The glue then becomes insoluble at the parts where hydrogen peroxid exists, and the plate is then further treated in the usual way.

In all cases other catalyzing substances, such as silver and the like, may be used instead of platinum.

Now what we claim is—

The process herein described of reproducing designs, which consists in causing an original to produce changes on a surface by chemical action, the degree of this action in the different points being controlled by catalyzing agents contained in the original, substantially as set forth.

In testimony that we claim the foregoing as our invention we have signed our names in presence of two subscribing witnesses.

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Witnesses:

RUDOLPH FRICKE,  
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