

UNITED STATES PATENT OFFICE.

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PHOTO-CHEMICAL PRINTING.

SPECIFICATION forming part of Letters Patent No. 423,849, dated March 18, 1890.

Application filed December 3, 1888. Serial No. 292,524. (No specimens) Patented in England February 2, 1887, No. 1,681, and November 21, 1887, No. 16,003; in Austria-Hungary December 1, 1887; in Belgium December 15, 1887, No. 79,780; in Italy January 19, 1888, XLIV, 474; in France February 15, 1888, No. 187,261, and in Spain April 30, 1888, No. 7,707.

To all whom it may concern:

Be it known that I, WILLIAM WILLIS, manufacturer, a subject of the Queen of Great Britain, and a resident of Bromley, England, have invented new and useful Improvements relating to Photo-Chemical Printing, (for which I have obtained patents in the following countries: Great Britain, No. 1,681, dated February 2, 1887, and No. 16,003, dated November 21, 1887; France, No. 187,261, dated February 15, 1888; Belgium, No. 79,780, dated December 15, 1887; Austria-Hungary, dated December 1, 1887; Italy, dated January 19, 1888, No. 474, Vol. 44, and Spain, No. 7,707, dated April 30, 1888,) of which the following is a specification.

My invention has for its object the production upon paper or other surfaces of photographic pictures or images in platinum—that is to say, pictures or images of which the coloring matter or pigment is platinum. It differs from the processes of photo-chemical printing described in the specifications of my former British patents, in which processes (as far as they relate to platinum) the paper or other surface is coated with a solution of a salt of platinum, and sometimes other salts, and also with a solution of ferric oxalate. These solutions are applied either separately or mixed to the paper, and in all cases the sensitive coating of the paper contains a salt of platinum and a ferric salt. After exposure to light the prepared surfaces are treated with one or other of the developing solutions described in the said specifications.

Hitherto no means have been known by which the salt of platinum could be employed entirely in the developer or developing solution, instead of wholly or partly in the sensitive coating of the paper or other surface, as above set forth. I have, however, now discovered a process by which I can accomplish this result. For this purpose I apply to paper or other suitable material which has been rendered sensitive by a coating of ferric oxalate and afterward exposed to light under or behind a negative or other suitable screen a developer containing salts of platinum and certain soluble phosphates, (or other salts, in which the ferrous oxalate image produced by

exposure to light is insoluble, or nearly so,) with or without the addition of potassic oxalate, potassic tartrate, ammoniac citrate, or other salts which tend to increase the rapidity and vigor of the development, or by always securing the presence of a salt of lead or of mercury, either in the sensitive coating of ferric oxalate applied to the paper or in the platinum developing-bath. The use of phosphates in this bath may be dispensed with; but in these cases the developing-bath must always contain, together with the platinum salt, a salt of oxalic, citric, or tartaric acids, or mixtures of these or other substances which aid in the reduction of the metal from the salt of platinum by the ferrous image produced by the action of light. By these improved processes I avoid the necessity of using salts of platinum in the sensitive coating of the paper or other surface. I thereby greatly diminish the cost of the process and can obtain good results without heating the developer. Moreover, I obtain a slower developing action, so that it is possible to watch the progress of development and to arrest it at any desired moment by washing the print in a solution of acid.

For the sake of clearness in the following description I will divide the same into heads.

First head. According to one part of my present invention I use paper, wood, woven fabric, or other material, the surface of which I prepare and render sensitive for photographic purposes by the application of a coating or coatings containing ferric oxalate with (or without) the addition of a salt of lead or of mercury, or mixtures thereof, and without any salt of platinum. I first prepare the paper or other surface by the use of this coating, as hereinafter specified. I then expose it to light under or behind a negative, and then develop the picture by means of one of my improved developing solutions hereinafter specified, or other suitable solution containing a salt of platinum. For preparing or coating the paper or other material I employ for ordinary purposes an aqueous solution of ferric oxalate, containing in each fluid ounce about sixty (60) grains of ferric oxalate, $\text{Fe}_2(\text{C}_2\text{O}_4)_3$; but I may use less or more of the

latter, according to the result desired to be obtained. I am of course aware that there are other salts of iron sensitive to light; but the oxalate is the best for my purpose. I sometimes mix or dissolve in the ferric oxalate a salt of mercury or of lead or a mixture of these salts. For instance, I dissolve in one fluid ounce of the ferric-oxalate solution above described from one grain to three grains of mercuric chloride; or I apply solutions of a salt of lead or mercury or mixed solutions of these salts to the paper or other surface, either previously or subsequently to coating the same with ferric oxalate. I find the mercuric salt very useful where a warm tone or effect somewhat resembling that of sepia is desired. Mercuric salts tend to increase the vigor of the developed images. Lead salts have the same tendency, especially when acid in conjunction with mercuric salts is used. I do not confine myself to aqueous solutions of the above-named salts. The paper thus coated, after being dried, is ready for use. If two coatings are applied to the paper or other surface, it is usually better to dry the paper between the application of the first and second coatings. After its exposure to light under or behind a negative I apply to the paper the developing solution.

I prepare an improved developing solution or developer as follows—that is to say, I use solutions of various soluble phosphates. I have been most successful with the following, viz: the monosodic or disodic, the monopotassic or dipotassic, or the monoammonic or diammonic orthophosphates, or mixtures or combinations of these salts with one another, and with or without the addition of other salts, such as potassic oxalate, ammoniac citrate, and others. In all cases I add to these solutions or mixtures of solutions a salt of platinum. I mix a solution of this salt with the above-named solutions, or I dissolve the platinum salt in them. I usually prepare this developing solution as follows—that is to say, I dissolve in one fluid ounce of water one hundred (100) grains of dipotassic orthophosphate, forty (40) grains of potassic oxalate, and ten (10) grains of potassic chloro-platinite; or I may make it in another manner, viz: by dissolving in one fluid ounce of water one hundred (100) grains of diammonic orthophosphate, thirty-five (35) grains of ammoniac citrate, and ten (10) grains of ammoniac chloro-platinite; or I make similar developing solutions with the salts previously mentioned. I make, also, developers containing only phosphates and salts of platinum—that is to say, I may make a developer by dissolving in one ounce of water about one hundred (100) grains of monopotassic or dipotassic orthophosphate or mixtures of these salts and ten (10) grains of potassic chloro-platinite.

Second head. In some instances I modify the above-described process in such a manner that I am enabled to entirely dispense with the use of phosphates. For this purpose

it is necessary to insure the presence or contact of a salt of mercury or of lead with the image or picture at the time of its development by the platinum solution. I sometimes adopt the following method—that is to say, I coat paper or other material with ferric oxalate, together with a salt of mercury or of lead, or both. Then I expose the coated surface to light under or behind a negative or other suitable screen, and then develop the ferrous image produced by the action of light with a solution containing a salt of platinum, together with a salt of oxalic or citric or tartaric acid or mixtures of these or other substances, which aid in the reduction of the metal from the salt of platinum by the ferrous image produced as aforesaid; or I adopt the following method, viz: I use a surface sensitized by ferric oxalate alone, and then, after exposure to light, develop the picture or image with a developing bath or solution containing one or more of the above-named salts or substances, which aid in the reduction of platinum in the manner aforesaid, together with a salt of platinum, and also a salt of lead or of mercury, or both, but in this case, preferably, the salt of lead. It will be observed that the lead or the mercury, one or the other of which is in all cases essential in the practice under the second head of my invention, is in the one case present in the sensitive coating of the paper before its exposure to light, and in the other case is wholly in the developer; but for some purposes I use a salt of mercury or of lead both in the sensitive coating of the paper and in the developer.

In practicing my invention according to the first method described under the second head of my invention I coat the paper or other surface with ferric oxalate, (or with a compound or mixture of the same and other oxalate of an alkali metal,) together with a salt of lead or of mercury or of both. The salts of lead which I find best for my purpose are the nitrate and chloride. If I use salts of mercury, I employ only the mercuric salts, and of these I prefer mercuric chloride. The ferric oxalate and the lead or mercury salt can be applied together in one solution, or the said salts may be applied separately in solution to the paper or other surface. I usually apply them in one solution. When they are applied separately, it is preferable to dry the paper or other surface between the coatings. In some instances I employ an aqueous solution of ferric oxalate containing in each fluid ounce about sixty (60) grains of the oxalate, $\text{Fe}_2(\text{C}_2\text{O}_4)_3$, more or less, according to the result desired to be obtained, and I add to or dissolve in each ounce of this solution one (1) grain of plumbic chloride and one (1) grain of mercuric chloride. I sometimes omit the lead salt from this solution and increase the quantity of the mercuric salt—that is to say, instead of one (1) grain of mercuric chloride I use two or more grains of this salt. The paper thus coated, after being thor-

oughly dried, is ready for use. After its exposure to light under or behind a negative or suitable screen I apply to it the developing solution. I prepare this developing solution with
 5 potassic oxalate and potassic chloro-platinite. I prefer to use an aqueous solution of these salts containing in each fluid ounce about ninety (90) grains of potassic oxalate and nine (9) grains of potassic chloro-platinite;
 10 or I use for developing an aqueous solution containing in each fluid ounce sixty (60) grains of ammonic tartrate and eight (8) grains of ammonic chloro-platinite; or I make developing solutions with any of the other
 15 salts or substances hereinabove mentioned as applicable for this purpose, or with other salts which tend to aid in the reduction of the platinum salt by the ferrous image produced by the action of light.

20 In practicing my invention according to the second method under the second head of my invention hereinbefore specified, I first apply to the paper or other surface a coating of an aqueous solution containing about sixty
 25 (60) grains of ferric oxalate in each fluid ounce of solution. I then dry the coated paper, and then, after exposing it to light under or behind a negative, apply to it the developing solution. For this developing solution I sometimes employ an aqueous solution
 30 containing in each fluid ounce about ninety (90) grains of potassic oxalate and nine (9) grains of potassic chloro-platinite. To this solution I add a solution of a salt of lead, preferably the acetate, until a permanent precipitate begins to form. If I use a salt of mercury instead of a salt of lead, I prefer the mercuric chloride, of which I dissolve (or
 35 add) about five (5) grains in each fluid ounce of the said solution. The salts of mercury do not in all cases insure a monochromatic tone in the picture, but in other respects they afford good results; or I use a developing
 40 solution containing a salt of platinum and a salt of lead or of mercury and one or more of the other salts of oxalic acid, or of salts of citric or tartaric acids; but when a salt of lead is employed there must be no salt used in the developer, which would entirely prevent
 45 the solution of the lead salt. These developing solutions containing lead or mercury salts, or both, can also be used for developing photographic pictures or images on paper and other surfaces which have been
 50 coated with ferric oxalate, together with a salt of lead or of mercury. I sometimes apply the constituents of the developer separately or in two solutions to the sensitive surface after it has been exposed to light. In this
 55 modification of my process I first apply a solution of plumbic acetate or of mercuric chloride to the said surface and then quickly, without washing or drying the surface, apply to it in solution the remaining constituents
 60 or ingredients of the developer.

The salts of platinum which I prefer to use in the developers (described in this specifica-

tion) are the platinous salts—viz., the ammonic, potassic, and sodic chloro-platinites, or the ammonic, potassic, and sodic bromo-platinites, or mixtures of these salts; but in some instances I use a small quantity of a platinic salt, such as the ammonic, potassic, or sodic chloro-platinate. The sensitizing or coating
 70 solution is applied to the paper or other surface by spreading it over the same with a pad of cotton, wool, or woven fabric, or by a brush, or by other means known to photographers as suitable for the purpose.

The developing solution is applied to the
 80 paper or other surface (after the same has been exposed to light under or behind a negative or other suitable screen) by pouring it over the same or by immersing the paper therein, or by floating the paper thereon, or
 85 by means of a brush or otherwise. It is preferably applied cold; but in cases where the application of heat will not decompose the solution it may be applied hot. A cold solution usually takes longer to effect the develop-
 90 opment of the picture than a hot one. The strength of the solution may be varied. Usually the best results are obtained by strong solutions of the phosphates and other salts. The platinum salt will ordinarily be used in
 95 the proportion of from five to ten grains of the salt to one fluid ounce of the developer.

What I claim is—

1. The herein-described process or method of photo-chemical printing, consisting in first
 100 sensitizing the surface of the paper or other material with a sensitizing solution containing a ferric salt free from platinum, then exposing the surface to light, then developing the picture or image by the use of a develop-
 105 ing solution containing a salt of platinum, all substantially as set forth.

2. The method or process of photo-chemical printing, consisting in sensitizing the surface
 110 of paper or other material with a sensitizing substance free from platinum, then exposing the surface to light, and then developing the picture or image by means of a developing solution containing a salt of platinum, and
 115 with a salt of mercury in the presence of or in contact with the image or picture during the development, substantially as described.

3. The method or process of photo-chemical printing, consisting in sensitizing the surface
 120 of paper or other material with a sensitizing substance free from platinum, then exposing the surface to light, and then developing the picture or image by means of a developing solution containing a salt of platinum, and
 125 with a salt of mercury and lead in the presence of or in contact with the image or picture during the development, substantially as described.

4. The method or process of photo-chemical printing, consisting in sensitizing the surface
 130 of paper or other material by means of a solution containing ferric oxalate or its compounds and a salt of mercury, then exposing the surface to light, then developing the picture or

image by the use of a developing solution containing a salt of platinum, substantially as specified.

5 5. The method or process of photo-chemical printing, consisting in sensitizing the surface of the paper or other material with a sensitizing solution containing ferric oxalate or its compounds, then exposing the surface to light, then developing the picture or image
10 by means of a developing solution containing a salt of platinum, together with a salt of mercury, but free from any phosphate.

15 6. The herein-described photo-chemical printing-surface, consisting of paper or other material having its surface sensitized with a ferric salt or compounds thereof and a salt

of mercury, but free from platinum, substantially as and for the purpose set forth.

7. The herein-described photo-chemical printing-surface, consisting of paper or other material having the surface sensitized with ferric oxalate or its compounds and a salt of mercury, but free from platinum, substantially as and for the purpose set forth.

Intestimony whereof I have hereunto signed
my name in the presence of two subscribing witnesses.

WILLIAM WILLIS.

Witnesses:

DAVID YOUNG,
A. E. NIXON.