UNITED STATES PATENT OFFICE.

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SENSITIVE PHOTOGRAPHIC PAPER AND PROCESS OF MAKING THE SAME.

1,120,580. Specification of Letters Patent. Patented Dec. 8, 1914.

No Drawing. Application filed September 22, 1913. Serial No. 791,021.

To all whom it may concern:

Be it known that I, WILLIAM WILLIS, a subject of the King of England, and residing in Brasted Chart, Kent, England, have invented certain new and useful Improvements in Sensitive Photographic Paper and Processes of Making the Same, of which the following is a specification.

This invention consists in improvements in or relating to photographic paper and method of making the same, and the expression "paper" in this specification is used to include paper, textile fabrics, wood, and other surfaces suitable for receiving photographic prints.

The principal object of this invention is the production of a photographic printing paper having a coating or surface sensitive to light and containing salts of iron, silver and platinum, which paper after exposure to light under a negative and subsequent development shall yield an image composed of silver and platinum, the platinum constituent of such image being variable in quantity in some proportion to the amount of platinum salt used in the sensitive coating of such paper. Thus the said paper may be produced either so as to give images composed of silver with very little platinum or images composed of silver with an increased proportion and quantity of platinum. And in practice the quantity of platinum in the image may advantageously be so increased until a point is reached where such image may be considered permanent. This point may be defined as the point where the image in platinum remaining after the silver content of the original silver and platinum image has faded, or has been removed, will of itself satisfactorily represent the gradation and retain all of the detail which existed in the original silver and platinum image before its silver content had faded or had been removed.

A further object of this invention is to secure such permanent residual images in platinum as herein before described by the employment of a quantity of platinum salt in the coating of the said printing paper less than that used in the platinotype process. And other objects of the invention are that such photographic printing paper shall be easy of manipulation in weakened ordinary daylight; shall require only a moderate exposure to light and shall remain in good condition during storage; and further that the images produced on such paper shall require no subsequent toning.

This invention is based on the discovery I have made that the reduction of silver chlorid by a solution of ferrous oxalate in potassium oxalate is greatly facilitated, increased in rapidity and made more complete, by placing in contact with this silver salt a small quantity of potassium chloroplatinite before the reducing agent (ferrous oxalate) is applied to the silver salt. And I have found that the only salts of platinum of value in thus aiding in the reduction of silver chlorid by ferrous oxalate are salts of chlorin and platinum that is to say chloroplatinites or chloro-platinates, salts which are also described as platino-chlorids or platini-chlorids. And I also find platinic chlorid to be of value. The salts of platinum just named are themselves reducible by a solution of ferrous oxalate and when one of these salts is used as above described to aid in the reduction of silver chlorid it will be reduced together with the silver salt and both platinum and silver will be liberated. This effect of platinum salts in aiding the reduction of silver chlorid can be easily shown by a purely chemical method but perhaps more readily by a practical trial on paper in the manner following: If the paper is first of all coated with silver chlorid and then with ferric oxalate, then exposed to light under a negative and then developed on potassium oxalate it yields only a poor image, but if in addition to the silver chlorid and ferric oxalate the coating is made to contain a small quantity of potassium chloro-platinite, then on exposure and development a stronger image of blackish color will be obtained; and it has been proved that the intensity of this image is due mostly to the increased reduction of the silver salt and only slightly to the reduction of the small quantity of platinum salt used in this experiment. One of the methods in which this discovery is applied in this invention to the production of an improved photographic printing paper is as follows:—The paper first of all receives a coating of silver chlorid which may be applied or attached to the surface as an emulsion in gelatin or other suitable medium or formed on the surface by the well known process of double decomposition. This

coating of silver chlorid should be free from other salts of silver. The coated surface is then again coated with a solution of ferric oxalate in which is dissolved some potassium chloro-platinite (K_2PtCl_4). After the paper has been dried, it is exposed to light under a negative. The action of light through the negative forms on the sensitive coating of the paper a faint image consisting mainly of ferrous oxalate. This exposed paper is now immersed in a solution of potassium oxalate which quickly commences to dissolve the ferrous oxalate forming the image, but this solution of ferrous salt in potassium oxalate is a strong reducing agent. Now salts of silver and platinum are in contact with the ferrous image on the paper and as this ferrous image is dissolved by the application of potassium oxalate, the resulting solution of ferrous salt reduces these salts of silver and platinum "*in situ*" forming or yielding an image composed of silver and platinum more or less in the metallic state and coinciding with the position of the original image of ferrous oxalate. This final image composed of silver and platinum is of a black tone agreeable to the eye and does not require toning. All that now remains is to dissolve out the unaltered salts from the paper in any suitable way.

In the production of this photographic printing paper it is essential to the invention that the salt of silver employed shall be the cholrid (or bromid) and not a salt of silver like nitrate and others which will decompose the platinum salt.

In my previous British Patent No. 2011, dated 5th of June, 1873, the object of which was to obtain photographs or pictures in which the image should consist of platinum, iridium or gold the complete specification (Example 2) gave a method somewhat similar in description to the method described in this invention. In that method paper was coated with silver nitrate. In practice it was found that the developed images on such paper contained very little metallic platinum, that they were very variable in quality and often required subsequent toning to render them of value. The process was unsatisfactory and was quickly abandoned. The most important distinction between the method employed in 1873 and that used in this invention lies in the fact that in the 1873 method of coating paper the platinum salt is decomposed by silver nitrate, whereas in this invention the platinum salt and silver chlorid do not suffer material mutual decomposition and remain as such in the finished paper prior to the process of development.

The following is a description of one of the methods adopted for coating paper according to this invention: I first apply to a sheet of plain paper such as is made for the platinotypé process, a coating of silver chlorid by the well known method of double decomposition the solutions used for this purpose being potassium chlorid and silver nitrate. The potassium chlorid must be in excess so as to secure a complete decomposition of the silver nitrate. The potassium chlorid solution is made by dissolving 5 grams of potassium chlorid in 100 cubic centimeters of water and the silver nitrate solution is made by dissolving 5 grams of silver nitrate in 100 cubic centimeters of water. After the coating of silver chlorid has been formed on the paper by the use of these solutions the paper surface is usually washed in water in order to remove soluble salts. But instead of applying this coating of silver chlorid to the paper by the method of double decomposition I sometimes make use of an emulsion of silver chlorid in gelatin or other suitable medium and apply such emulsion to the paper by one of the usual and well known methods. The second coating solution now to be applied to the paper I prepare by dissolving a small quantity of potassium chloro-platinite in a solution of ferric oxalate, this ferric oxalate solution being such as is usually employed in the platinotype process, for example it may be prepared by making a 20% solution of dry ferric oxalate in water. A stronger or weaker solution than this may however be employed according to the paper that is used and the effect desired. Now in order to prepare the second coating solution I dissolve in 500 cubic centimeters of the ferric oxalate solution of about the strength described above one gram or less up to six grams or sometimes more of potassium chloro-platinite. If the object be to form the image mainly of silver I dissolve say one gram of potassium chloro-platinite in the ferric oxalate solution but if the object be to make an image which will have or contain a permanent residual image of platinum I dissolve say six grams of this salt in 500 cubic centimeters of the ferric oxalate solution. The second coating solution is applied either by brushing the solution over the paper previously coated with the silver chlorid or by floating the paper on the solution or by other suitable means. The coating is finally well dried in a current of warm air or before a fire or in any suitable way. The paper thus coated is now ready for use. It is first of all exposed to light behind a negative or other suitable screen and then immersed in a developing solution, made by dissolving 453 grams of potassium oxalate in 1812 grams of water. In about one minute development is usually complete. The developed print is then removed to a clearing bath made thus: potassium bisulfate 85 grams, potassium oxalate

14.2 grams, water 2840 grams. In this bath it should remain from ten to fifteen minutes and then it is well washed in several changes of water. Finally the print is "fixed" in a "hypo" solution made by dissolving 28.4 grams of sodium "hyposulfite" in 284 grams of water. The print is finally washed in several changes of water.

Other methods and salts may be used for developing and clearing or "fixing" the prints but the method described is an excellent one.

In preparing the said photographic printing paper I sometimes vary the operations described above or invert their order, that is to say, I may change the order in which the various salts are applied to the paper. For instance, instead of applying the potassium chloro-platinite salt mixed in solution with ferric oxalate I sometimes apply the potassium chloro-platinite dissolved in water or in any suitable solvent as a separate coating which I apply usually between the coating with silver chlorid and the coating with ferric oxalate. And I sometimes employ for coating the paper an emulsion of silver chlorid in a suitable medium in which is dissolved the requisite quantity of platinum salt and of ferric oxalate.

I sometimes apply the sensitive coating to other surface than paper, for instance to cotton or linen fabrics, to silk fabrics, to wood, &c.

In preparing the said photographic printing paper or other surface I sometimes employ other salts than those named for instance in the coating of the paper I may use the silver bromid instead of the silver chlorid but I usually prefer the latter salt. And instead of the potassium chloro-platinite I sometimes use the sodium or ammonium chloro-platinite or other suitable chloro-platinites or the potassium, sodium or ammonium chloro-platinate or platinic chlorid but of these salts I prefer as the most generally useful the potassium chloro-platinite. And instead of a solution of ferric oxalate I sometimes employ a solution or solutions of the double salts of ferric oxalate with potassium sodium or ammonium oxalate or other suitable oxalate, or a solution of ferric citrate or its double salts, or mixtures of solutions of any of these with a solution of ferric oxalate; these equivalent solutions are hereinafter included in the term "ferric oxalate." And in the formation of the coating of silver chlorid on the paper by means of double decomposition I do not confine myself to the salts named in the above described process, namely potassium chlorid and silver nitrate but I may use other salts which by their mutual decomposition will precipitate silver chlorid.

I do not restrict myself to the exact proportions or quantities of the chemical salts used in the above described process, as these proportions and quantities may be varied within certain limits according to the results desired to be obtained or to other conditions. I do not confine myself to the use of aqueous solutions of the chemicals hereinbefore referred to, as the salts may be dissolved and used with any suitable solvent.

I have further found that particularly advantageous results can be obtained in the above process by using paper the surface of which has been parchmentized by treatment with acid or by other well known means. The paper is preferably coated or treated on each side with sulfuric acid sufficiently strong to attack the paper; the paper is well washed in water to free it from acid and is then dried. The acid is not left on long enough to penetrate the paper, the aim being to get a film of altered paper on each side.

What I claim as my invention and desire to secure by Letters Patent is:—

1. The herein described process for making a photographic printing paper which consists in coating the paper with a haloid salt of silver and with a salt of platinum and chlorin and with ferric oxalate; substantially as described.

2. The herein described process for making a photographic printing paper which consists in parchmentizing the surfaces of paper, coating the paper with a haloid salt of silver, with a salt of platinum and chlorin and with ferric oxalate; substantially as described.

3. The herein described process for making photographic printing paper which consists in coating the paper with silver chlorid, potassium chloro-platinite and with ferric oxalate; substantially as described.

4. The herein described process for making a photographic printing paper which consists in coating the paper with silver chlorid by the method of double decomposition and with potassium chloro-platinite and with ferric oxalate; substantially as described.

5. The herein described process for making a photographic printing paper which consists in coating the paper with silver chlorid by applying thereto solutions of silver nitrate and potassium chlorid and with potassium chloro-platinite and with ferric oxalate; substantially as described.

6. The herein described process for making a photographic printing paper which consists in parchmentizing the surfaces of the paper by treating them with sulfuric acid, and washing and coating the paper with silver chlorid with potassium chloro-platinite and with ferric oxalate; substantially as described.

7. Photographic printing paper coated

with a haloid salt of silver, a salt of platinum and chlorin and ferric oxalate; substantially as described.

8. Photographic printing paper coated with silver chlorid, potassium chloro-platinite and ferric oxalate; substantially as described.

9. Photographic printing paper which consists of parmentized paper coated with silver chlorid, potassium chloro-platinite and ferric oxalate; substantially as described.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

WILLIAM WILLIS.

Witnesses:
WILLIAM H. BALLANTYNE,
HARRY S. BRIDGE.