PLATINOTYPE:

ITS PREPARATION and MANIPULATION.

by

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CHAPTER I.

Introduction

In treating the subject of printing with salts of platinum, one cannot fail to remark that the methods at present in use have nothing in common with the ordinary process of silver printing; that is to say, the platinum salt is not darkened, per se, by mere exposure to light, as is the case with the chloride or other salts of silver, but requires the intervention of some other chemical reagent.

In reviewing, therefore, the previous experiments that have led up to the modern system of platinotype, it will be convenient to divide them into three heads, viz.: 1st, where the actual platinum salt darkens by exposure to light; 2nd, where some agent is added to make the latent change in the platinum itself visible; and 3rd, where some other salt, capable in itself of deoxidation by light, is first used, and will throw down metallic platinum from solutions of the salt.

I

Platinum salts, per se, are but slightly acted on by light. An early experimenter on the subject appears to have been Sir John Herschel, who gave to the British Association at Oxford, in 1832, an account of the action of light on a solution of chloride of platinum neutralized with limewater. Such a solution, when exposed to light, clouded, and threw down a white, or, with excess of platinum, a yellow precipitate. Johannsen obtained the same reaction with a solution of soda and baryta water added to the platinic chloride ($PtCl4$). Herschel noticed that it was only the violet end of the spectrum that had this reducing action; when the mixture was protected by a solution of potassium bichromate or tincture of rose leaves in sulphuric acid, no change took place. Gehlen found that an ethereal solution of platinic chloride, when exposed to light, first turned a yellow colour, and eventually threw down metallic platinum in the form of a thin film on the sides of the vessel. Dobereiner obtained analogous effects by mixtures of platinic chloride and solution of sodium tartrate, tartaric acid, formic and oxalic acids. He also appears to have used the double platinous salt, chloro-platinite of potassium.* Robert Hunt made a good many experiments on the action of light on the platinum salts; mixing a solution of platinic chloride and cyanate of potassium, he obtained a double percyanate of potassium and platinum, and on brushing this mixture on paper and exposing it to sunshine, he found that after a prolonged exposure only a very faint image resulted. He noticed that the chemical action took place first in the blue ray, then going on through the violet, but not extending much beyond the visible spectrum. He remarked, however, a curious darkening in the yellow ray, which, on continued exposure, disappeared, and finally resulted in a bleaching effect.

With platinic chloride ($PtCl4$) washed on paper, some action certainly took place but it required the action of a deoxidizing agent to make it apparent. He made a good many experiments with this salt in conjunction with oxalic, tartaric, and formic acids, and some of the cyanogen compounds. The results varied but slightly, but were somewhat remarkable, as it appeared that sometimes the action of the solar rays was to darken, and sometimes to bleach the yellow colour of the salt. This, he thought, might have been due to the different quantities of the yellow and blue rays present during the different exposures.

He also tried experiments with the other platinic haloid salts, at the instigation of Sir John Herschel, but discovered nothing remarkable or any difference in behaviour.

From the above experiments it is evident that the action of light does cause a reduction of the platinic haloid salts, reducing them first to platinous haloid, and, on further exposure, to metallic platinum. The first action of light is apparently to bleach the paper, from the fact that the yellow platinic chloride is brighter to the visual nerves than the pinkish platinous chloride; but by prolonged exposure it becomes black from the deposition of finelyu divided metallic platinum. Pizzighelli and Hubl found, as was to be expected, that the presence of an easily oxidizable organic substance hastened this reduction, the blackening taking place more quickly when oxalic acid was present.

If the platinous salts be used, the result will be the same, leaving out, of course, the first step in reduction. These salts behave very much the same as the silver salt-that is to say, they are capable, according to Pizzighelli, of receiving a latent image, invisible at first, but which can be brought into evidence by the addition of suitable developing agents.

We have ourselves made some experiments on a printing-out process in platinum, employing the double salt formed by adding silver nitrate to platinous chloride. (The actual salt employed in our case was the chloro-platinite of potassium.) The double salt formed is of a yellow colour, and is, according to Lang, a chloro-platinite of silver ($PtCl_2AgCl$). Under the influence of light it darkens, but very slowly, to a pretty full black. The unaltered salt can be dissolved out by strong ammonia; the action is, however, too slow to have any practical value.

In conclusion, we may remark that a direct reduction of either platinic or platinous salts, per se, is not practicable as a printing process; we can therefore dismiss this division, and proceed to the second, where a developing agent is used to reveal or obtain the metallic deposit.

II

Hunt found that a neutral solution of platinic chloride ($PtCl_4$), mixed with cyanate of potassium, and after exposure washed with a solution of mercurous nitrate, gave a pretty, though delicate, positive picture. It, however, subsequently faded even in the dark.

If paper prepared and exposed in the same way were washed over with nitrate of silver, a faint positive image was formed; on re-exposure to light, the hitherto unacted on portions blackened, whilst the already reduced portions remained light, and a fairly good negative resulted.

If this paper be washed over with mercurous nitrate first, it assumes a yellowish brown tint. Exposed to sunshine, it gives a very peculiar picture, which will be either negative or positive, according to the depth of colour, which is exceedingly capricious, that is produced. The exposed portions often pass into a beautiful vermilion colour, which, however, fades with some rapidity, leaving the ground of the paper a buff or ruddy brown.

Paper washed with percyanate of potassium and chloride of platinum, and then with nitrate of silver, darkens to a well- defined lilac tint. If mercuric chloride be added, even with an exposure of fifteen minutes no change is apparent, but on treating it with a strong ammonia a picture of intense blackness on an iron-grey ground is at once formed.

All the above results of Hunts were, however, found to be unstable, and, after being kept in a portfolio some time, completely faded. It is worthy of remark, however, that although the picture on the platinum paper had disappeared, where they were in contact with argentine papers a good image, dark on a light ground, had been transferred to these latter.

It is difficult to know how much of the above results is to be ascribed to platinum, and how much to the other metals employed.

Considering the great stability of metallic platinum, it can hardly be allowed that when once formed it could easily be reoxidized. That platinum salts, however, are capable of development is a known fact. Gehlen, as far back as 1834, showed that an ethereal solution of platinum, after a short exposure to light, was reduced by ferrous sulphate, and later Pizzighelli and Hubl showed that paper washed with chloro-platinite of potassium and oxalic acid, after a short exposure to light, was reduced by the action of a cold solution of ferrous oxalate. But as in our first division, the latent image formed by the platinum salts does not offer a practical printing method, and we now come to our third and somewhat analogous division, where the metallic platinum is reduced from its salts by the application of some substance which in itself is incapable of causing reduction, but gains this property by exposure to light.

III.

It is in this division that we find all the present known systems of printing in platinum. The rationale of the process lies in the fact that, whereas the salts of platinum are unaffected by a per-salt of the heavy metals, they are reduced when in contact with a proto-salt, to which may be added some other agent, which, incapable itself of reducing the platinum, still accelerates or facilitates the reduction of this metal. In order that this fact may be practically made use of for photographic purposes, it is evidently necessary that a substance be found which can be reduced by the action of light from the per to the proto state, in which case the future image will be a positive. For this purpose the salts of the heavy metals seem particularly fitted, such as iron, uranium, or silver. As all know, the chlorides or other salts of these metals, on exposure to light, are reduced either to some lower oxide or the metal itself; the parts therefore so acted on by light will have the power, if platinum be presented to them, of precipitating it from certain of its salts.

The Use Of Silver For Forming The Provisional Image

Although not the first used, it will perhaps be better to treat of the silver salts first, as they still serve as a basis for a form of platinum printing. We allude, of course, to toning by means of salt of platinum. De Carranza* has the reputation of being the first to describe this method, but the process cannot be said to have been very favourably received. At the same time, C. Poupat (Lumiere, Feb., 1856) used double chloride of platinum and sodium, and for albumenized paper the double hyposulphite of platinum and soda.

Carranza found many imitators, who each proposed platinum toning formulas which differed but slightly from his own, Baldus (Photographic Notes, June 1, 1857) uses neutral chloride of platinum instead of sel dor for B. Evrards printing process. Haackman* made the remark that prints on matt surface paper toned much more readily than those on albumenized. He also recorded the fact that generally platinum was less active than gold. Watt** states that prints so toned do not fade, although exposed continuously to light for years. Gwenthlian *** made some experiments in platinum toning, and records the fact that alkaline solutions gave brown tones, whereas acid ones produced bluish colours.

Platinum toning, moreover, was somewhat largely used in the burnt-in enamel processes. The image is here formed in silver suspended in collodion; this image is toned by platinum till the whole of the silver is replaced by platinum. The plaque is then fired, the collodion is all vaporized, and the black metallic platinum left burnt in on the porcelain. This process is interesting, as it appears to show that the silver is completely replaced by the platinum, for if any of the former salt were left in the collodion on the plaque, the image would burn out of an unpleasant, greenish colour, quite destroying the beauty of the enamel.

In 1864 (Photographic News, 1864, p. 184), a Dr. Maugham appears to have made some experiments in platinum toning, using the ordinary bichloride, but suggested at the same time the use of the double salts of platinum and the alkaline chlorides. Reference is also made (ibid.,p.184) to some prints produced by Captain Sellon, who is stated to have experimented with the sodio-chlorides of platinum, rhodium, and iridium, but no details are given.

With these exceptions, however, platinum toning processes have never been in favour with photographers. Their action is very slow, the results are uncertain, and inferior at the best to those obtained by gold. In fact, it is by no means an easy matter to obtain good results when the ordinary platinic chloride is used. This salt is found under many aliases at the dealers, sometimes being called bichloride (a relict of the old chemistry), sometimes tetrachloride, and sometimes with the safer title of simply chloride of platinum. It really appears to be chloro-platinic acid ($PtCl4 2HCl+16H20$), the real platinic chloride, $PtCl4$, being insoluble in water, according to Pizzighelli. Watt states that when pure it is soluble in water, in which we agree with him. It is, probably, the presence of the hydrochloric acid, and then reacidify with nitric acid.

In 1889, Mr. Lyonel Clark described a practical toning process with platinum, using for this purpose the chloroplatinite of potassium. This was described and specimens shown at a meeting of the Camera Club. As the process will be described fully further on, we will not now allude to it any further.*

Soon after this date Mr. Valentine Blanchard brought out his platinum process. He has not, however, described his method of working, which he keeps a secret. His process does not appear to differ very materially from the ordinary form of platinum toning. He prepares a special matt surface paper, which appears to be heavily salted and sensitized. The image is considerable over-printed, and then toned in his special solution. It may be that he uses one of the platinous instead of the platinic salts in his process.

There is another use of platinum, foreign to printing, however, but which is somewhat analogous to it, and that is the process of intensification by means of platinum. In these processes, as in the toning processes, the silver image is replaced or increased by platinum.

Eder and Toth* made a very close set of experiments on the action of platinum chloride on negatives produced by the wet process and developed with iron, using platinum solutions of different strengths and different degrees of acidulation. Generally speaking, they found but little difference in the results; 1 in 800 or 1000 is the strength they recommend, but a greater or less degree of concentration only quickens or slows the action, the final result being the same. With regard to the acidulation, hydrochloric, acetic, and nitric acids were tried; nitric worked the most quickly, and acetic the slowest, the proportions being 20 drops of nitric, or 30 glacial acetic, or 20 hydrochloric acids, added to each 500 cubic cent. of platinic chloride (1 in 800). Neutral baths gave no advantage, working more slowly than the acid ones. Some experiments that we have made with other platinum salts appear to confirm the above results, it being a curious fact that, whatever the degree of concentration, the final result was always the same.

In this process of intensification, the metallic silver is converted into chloride at the expense of the platinic chloride, which, in its turn, reverts to the metal. In this state, if the plate be treated with hypo, the silver chloride is dissolved out, and only the platinum left. In order to attain a still greater increase of density, Eder and Toth, instead of dissolving out the silver, converted it again into metallic silver by flowing over the converted negative a solution of ferrous sulphate. This operation they repeated several times, in order to still further increase the density, but found that their efforts were circumscribed, as, after two or three applications, the platinum black refused to adhere any longer to the image, but was washed away. They also tried the possibility of combining the platinum and iron into one solution, so as to require only one operation; they succeeded fairly well, but the solution would not keep, the ferrous sulphate gradually decomposing the platinic chloride. In spite of these numerous and interesting experiments, platinum never attained any great vogue as an intensifier for wet plates.

With the advent of gelatine dry plates, Willis also proposed a system of platinum intensification. He converted the silver image into an oxalate of silver by treating it with ferric oxalate;* he then washed it, and flowed over it a solution of chloro-platinite of potassium. The action of this is to convert the silver oxalate into chloro-platinite of silver.

This silver chloro-platinite is then treated with the ferrous oxalate developer, which reduces it and the platinum, or at least a portion of this latter, to their respective metals. Unfortunately for the value of this process, platinum has the property of rendering gelatine completely insoluble and impermeable, causing irregularities, so that the process was soon dropped.

The Use of Metals Other Than Silver

Uranium and iron are so closely allied in their action that they may be taken together; however, iron has proved to be by far the most suitable salt, the uranium per-salt also appearing to slightly reduce the noble metals, so that the high lights are not easily kept pure.

The per-salts of iron have been used as photographic agents from the very dawn of photography. Even the old Niepce writes in a letter to his brother (June 16, 1816), that he had tried an alcoholic solution of ferric chloride, but had not succeeded, owing to the rapid deliquescence of the mixture.

The next worker in this line was Robert Hunt. In his first book on photography,* page 37, he mentions some experiments with the chlorides of gold and platinum on paper treated with an iodide of silver, but did not succeedfor causes we can now understandin obtaining any tangible results. Doubtless, too, many of the experiments we have described under our second heading may almost come under the present, expecially that with the per-cyanate of potassium, which has doubtless reduced itself to the proto state, and thus aided in reducing the platinum salt. That he knew of the powerful action that proto-oxalate of iron exerts on platinum is evident, for he describes some experiments he made in this direction, although, from the present state of our knowledge, we can see why he failed.

Whilst on the subject of the iron salts, we may here mention the chrysotype of Sir John Herschel,* who used a solution of ammonio-citrate of iron, the exposed portions of which had the power of instantly reducing gold or silver from their salts. Sir John Herschel does not appear to have tried this with platinum, or perhaps, what is more likely, he did try it and failed, and therefore left no record of his labours. After this, platinum, in conjunction with iron or uranium as a photographic agent, appears to have lain dormant until the advent of collodion gave a fresh impetus to the practice of photography.

The Duc of Luynes was the next person. In a communication to the French Photographic Society, November, 1859 (Photographic

News, vol.iii. p. 259), he describes a gold and platinum printing process. He states that his experiments were suggested to him by M. Poitevin, who had been making some experiments in a printing process by means of perchloride of iron and nitrate of uranium; the parts exposed to light were bleached by light, and on treating the print with gallic or pyrogallic acid only combining with that part of the iron that remained in the more oxidized state.

Re-discovering Herschel's chrysotype the Duke, reasoning that the less oxidized portion of the iron salt (the proto-salt) should reduce gold from its salts, added chloride of gold to the above mixture, and obtained, after some considerable exposure, a positive brown image from his negative. To verify the fact that it was the gold that formed the image, he exposed paper prepared according to Poitevins direction to light, and then passed it through the chloride of gold bath, thus absolutely repeating Herschels experiment with the same result.

Finding, however, that this process did not give him full enough intensity in the high lights, he added chloride of platinum to the iron solution in the paper; this was done empirically, since it was not then believed that the proto- salts of iron would reduce the perchloride of platinum. He says that the results, however, were very fine, giving vigorous iron-grey and black prints when, after exposure, they were passed through the chloride of gold bath. We should remark here, however, that it was not the iron that reduced the platinum; in fact, as the Duke states, the print, after coming out of the printing-frame, showed only a bleached image on a yellow ground; the most probable cause of the reduction was the gold solution. We ourselves, in some experiments, mixed some chloride of gold with the chloro- platinite of potassium, when instantly a dark precipitate, either of metallic gold or platinum, or probably both, was thrown down. Now, although terchloride of gold will not throw down perchloride of platinum, yet the latter salt was in the Dukes prints already reduced to a platinous salt, in which case, as our experiments show, it would have been thrown down in the metallic state.

The fact that the proto-salts of iron alone do not reduce platinic salts (or platinous salt, for the matter of that) is shown by an experiment of Mr. Williss, at the 1888 Conference of the Camera Club.* He took three test-tubes containing a solution of proto-salt of iron, and added chloride of silver to one, chloride of gold to another, and chloride of platinum to the third. Whereas in the first two the metals were instantly thrown down, in the third the solution remained unchanged. We have further repeated the same experiment with paper washed with potassio ferric oxalate; whilst chloride of gold was instantly reduced by the exposed portions of such paper, the platinic and platinous salts both remained practically unchanged.

From this it will at once be understood why the earlier experiments with platinum failed. According to Van Monckhoven, Niepce de St. Victor** also experimented exactly the same way as the Duc de Luynes. He is said to have exposed a piece of paper coated with uranium nitrate, and developed the scarcely visible uranous image with solutions of gold or platinum. But we should be inclined to doubt very much the fact that he obtained images by using platinum alone. Bollman also used platinum salts in the production of uranium images by applying a mixture of uranium and platinum to the paper, and developing or intensifying with gold; the reader will understand the reasons of the success of this process. He also first converted the uranous image into metallic silver, and then toned by means of platinum. This process was also described by Krone (Bull. Soc. Franc., 1882, April), but both these processes are so similar to the Duc de Luynes that the inventors can claim but little merit for them.

Merget, in 1873, was the next worker with platinum salts; he used a solution of platinum chloride mixed with one of ferric chloride and tartaric acid. The deliquescent ferrous salt formed, in conjunction with mercurial vapour, was said to complete the reduction of the platinum. This would doubtless be so, the mercury acting in a similar was to the gold, being first reduced itself, and then reducing the platinum. Besides mercury, Merget tried exposure to hydrogen, sulphuretted hydrogen, and the vapour of iodine. In his opinion the conditions of success in working this method depend not only on the more or less appropriate choice of sensitive substances, but also on the proper preparation and physical properties of the sensitive films. When prints are produced by the direct or indirect reduction of the salts of the precious metals, the vigour of tone produced depends, according to Merget, materially on the grain of the sensitive film. This may be obtained by the happy selection of the proper kind of paper, or by the addition of certain substances which, though in a state of fine crystals or powder, are yet insoluble, so that their particles nestle in between those of the sensitive substance. This process for the indirect production of the platinum image, as described by Merget, never seems to have got beyond the experimental stage.

In the same year as Merget described the above experiments, Mr. Willis brought out and patented his first platinotype patent (specification No. 2011, June 5, 1873).

Dr. van Monckhoven, in a letter to the Bulletin Belge (trans. Photographic News, 1880, p. 75), alludes to the researches of St. Victor, and says that he (Van Monckhoven) had before that date described in the old Bulletin Belge of 1863 a platinum process, in which he used oxalate of iron and ammonia, and developed the image with chloride of platinum, gold, or palladium. He states that these prints were found to fade. His claim to originality cannot, however, be admitted (see British Journal of Photography, 1887, p. 55), and his process is of no practical value.

Mr. Willis, in a paper delivered at the Camera Club Conference, 1888 (Camera Club Journal, 1888, vol.ii.p.49), states that, whilst experimenting with the reduction of metals by means of the ferrous salts, and expecially the ferrous oxalate, he was struck with the obstinate way in which the platinum salt refused to be thrown down; he came to the conclusion, however, that some chemical could be found that would aid this reduction, but for a long time his efforts were unsuccessful, till a note by a French chemist let him to try the neutral oxalate of potash. Considering the remarkable action that oxalic acid has in reducing the salts of gold, it was to be expected that he was working in the right direction. Experiment proved his surmises to be correct, for on adding the neutral oxalate to the ferrous oxalate, and then adding the platinum chloride, metallic platinum was instantly thrown down.

On this he based his first patent process, in which a solution of a salt of platinum, iridium, or gold, or a mixture of these, is applied to the surface of paper, wood, or some other suitable material, and dried; it is then coated with ferric oxalate or tartrate, again dried, and exposed to light under a negative; a faint brown image will appear, which, after being brushed over with a solution of potassium oxalate, turns a strong, intense black.

The following instructions were given by Willis:-

l. Coat a piece of paper with a solution of 1 part chloro-platinite of potassium in 48 parts of water. When it has been dried, dip the paper in a solution of 1 part nitrate of lead in 48 parts of water. Dry once more, and brush over with a solution of 1 part ferric oxalate in 8 parts of water, to which, in order to render the oxalate more soluble, a little oxalic acid has been added. After again drying, the paper may be exposed under a negative, and then put to float on a hot solution of potassium oxalate. Finally, it must be washed in a weak solution of oxalic acid in water, then in sodium hyposulphite, and lastly again in water.

2. Proceed as in the previous case, only substituting for the lead solution one of 1 part silver nitrate in 60 parts of water. When the prints are taken up from the weak solution of oxalic acid, they must be dipped either in a strong solution of ammonium chloride, or in a weak solution of the same salt, and then in a weak one of ammonia. Finally, rise well in water.

3. The paper is first dipped in a solution of 1 part platinic bromide in 40 parts water, then dried, then again dipped in a strong solution of ferric tartrate, and afterwards once more dried. It is now exposed beneath a negative, and the image thus obtained is developed by floating on a hot solution of potassium oxalate. Afterwards it is immersed in a weak solution of oxalic acid, finally rinsed in water, and dried.

Mr. Willis also introduced a new departure in using a platinous instead of a platinic salt from which to form his visible image. He says that after his discovery of the action of the oxalate of potash, he immediately tried the experiment of coating paper with ferric oxalate, and developing with the oxalate of potash and chloride of platinum, but the experiment was a failure, as he only got a slight reduction in the deepest shadows. It then occurred to him that a platinous salt-that is, one containing two atoms less of chlorine-should be more easily reduced, as the ferrous salt would have less work to do in splitting up the more unstable molecule, and, moreover, less of it would be required.

Mr. Willis states (Camera Club Journal, vol.ii.p.48) that at that time (1873) he was aware of, or had discovered, the following facts:-

1. Ferric oxalate as a sensitizing agent on which the light acts.
2. Salts of platinous chloride, from which the pigment platinum black was to be obtained.
3. Potassium oxalate, which conveniently may be termed the developing agent.
4. Salts of lead or mercury as aids to reduction.

The 1873 process, however, was soon found by Mr. Willis to be somewhat complicated and not very certain in its results, and in 1878 he obtained a new patent (No.2800, July 12, 1878). The chief point in this new process was the entire elimination of the silver salt, and, of course, the hyposulphite bath. He also made a new departure in adding chloro-platinite to the developing bath, as well as the surface of the paper. The following is a description of this process:-

Paper or any other suitable support is dipped in a solution of-

Water	30	parts.
Chloro-platinite of potassium	1	parts.

Ferric oxalate	4.5	part.
Lead chloride	0.13	part.

After being dried, the paper is exposed under a negative, and the image is brought out by floating on, or dipping in, a hot solution of-

Water	30	parts.
Potassium chloro-platinite	0.5	part.
Potassium oxalate	8	parts.

The print is then passed through a weak bath of oxalic acid, then washed and dried.

Willis states also in this specification that in place of the chloro-platinite of potassium he can use other salts of this metal, or the nobler metalsgold, palladium, and iridium either in the sensitizing mixture or in the developer, although he prefers the former salt. He also mentions the possible of using or substituting bichloride of mercury for chloride of lead.

Even this process does not appear to have contented Mr. Willis, for in 1880 he again applied for and obtained a patent for improvements in platinotype (No. 1117, March 13, 1880).

This patent is substantially the process now in general use, and known as the hot-bath process, and which will be fully described in its proper place. We shall, therefore, not allude to it any further here, beyond saying that the alteration or novelty consisted in applying the requisite amount of the platinum salt to the paper itself, and leaving it out of the developer altogether; the lead and silver salts in the sensitizing mixture were also abolished. By this means the process was simplified, and the danger of discoloration from the use of the lead and silver salts avoided.

This process, although but little taken up at first, gradually grew in the public favour, and at the present time a glance at any of the photographic exhibitions shows that the process is most largely used by both amateurs and professionals.

In the exhibition of the Photographic Society in 1880, only 15 examples out of 373 are described as being platinum printswe except some few specimens sent by the Platinotype Companywhereas in 1894 there were 175 out of the 382 on the walls (British Journal of Photography, 1894, p. 613).

Another process of platinotype printing is due to Captain Pizzighelli, Benjaluka, Bosnia, and was first described by him in the Photographische Correspondenz of October, 1887, and January, 1888. In this system Pizzighelli does away with the separate developing solution altogether, this being applied to the paper itself, by which means, as the ferric salt in the paper is gradually reduced by light to the ferrous state, it and the oxalate of soda in the paper react on the platinum salt, and the metal is produced during the exposure. This reduction, however, depends on the presence of moisture in the air, and, therefore, in dry weather glycerine or some hygroscopic substance has to be added to it. On removal from the printing-frame, the prints require to be merely soaked in weak hydrochloric acid to dissolve out the iron salts, and after a short washing they are completed. Papers prepared according to Pizzighellis formula are now obtainable from dealers, and as the process is a commercial one, we shall again refer to it in its proper place.

In 1888, Willis again appears with a new platinum process, which he first described at the Conference of the Camera Club, March 13, 1888 (vide Camera Club Journal, No.xvii.p.47; also No.xix.p.99; and No.xx.p. 103). This process, which was called the cold-bath process (not to be confounded with the cold-development process of 1892), did away with platinum in the sensitizing mixture, this salt being added to the developer instead. Paper for this process in not now in the market, but the prints produced by it were of great beauty. It is perhaps remarkable for being the first platinum process that gave rich brown blacks as distinguished from the yellow browns given by the sepia process. It could also be worked with the paper damped, the colour, indeed, being thereby much improved. The preparation of the paper appears to be a little uncertain, and with the advent of the 1892 cold- development process, which also permitted the obtention of rich tones, its manufacture was gradually dropped. The idea of this process was the saving of the costly platinum salt; but, unfortunately, the developing baths to which the platinum was added would not keep, the metal being precipitated therefrom after a time, and so the bath soon became useless. Unless, therefore, large batches of prints were treated at a time, it became really a more expensive process, and did not make the way it merited. The real cause, however, of the dropping of this brand of paper by the Company, is undoubtedly to be found in the fact that the 1892 process offered most of the advantages of the former one without its drawbacks, whilst being more easily manipulated, it was commercially better.

This latest process, which holds the field, together with the old hot-bath process, at the present day, was also first described by Willis at the Camera Club in the Conference of March 22, 1892 (see Camera Club Journal, No.1xix.p.53; and No. 1xxii.p.19). As this process together with the hot-bath are the processes in ordinary use at the present time, they will be fully described under their respective headings, and we will only say here that the improvements in the process consist in the fact that the developing solution is used at the ordinary temperature of the room, and that the development can be retarded to such an extent that considerable local manipulations of the print are possible. The bubbles and watermarks that so frequently spoilt hot-bath prints are in this process entirely avoided, as, if on the first application of the developer the prints are covered with bubbles, they entirely disappear on a second application. Like the platinum in the bath process, prints can be developed and printed in a damp state, and in addition the paper, according to the inventor, improves by keeping, at least up to a certain extent, gaining not only greater insolubility, but improving the value of the blacks.

The Researches of Burnett.

We have kept the researches of C.J. Burnett of Edinburgh distinct from other early experimenters, because of their varied nature and, from a chronological point of view, their importance. According to the numerous papers of this gentleman, that are to be found in Photographic Notes, Journal of the Photographic Society, Liverpool and Manchester Journal, and Photographic News, between the years 1857 and 1859, the amount of experiments made are extremely numerous, and embrace an examination of most of the salts known to be affected by light. But the only ones that interest us are those containing results obtained by means of platinum and the metals of that group. The first mention that we find of this gentlemans work is a record in Suttons Photographic Notes of a paper read before the Photographic Society of Scotland on February 10, 1857 (Photographic Notes, vol.ii.pp. 97,160 & 181). Burnett states that this paper was delivered before a meeting of the British Association held at Edinburgh in 1855, and the specimens referred to were shown at that meeting, the paper, however, not being published in the proceedings of the British Association. The basis of the processes described and shown was an uranium salt, preferably the tartrate, the proofs being developed with silver, gold, and platinum (the latter salt being queried in the article). In the same paper, however, he states that he had experimented in the direction of toning ammonio-nitrate of silver paper with platinum, palladium, and rhodium, but with- out success. In vol.V.P.83 of the Journal of the Photographic Society, Burnett describes prints, exhibited by him at the Exhibition at Suffolk Street, in January of that year, and states that they were the same as those shown at Edinburgh and at the British Association. He describes them as prints in uranium, developed with nitrate of silver, and toned with gold, platinum, and palladium. Other prints were shown, produced on albumenized paper sensitized with ferric nitrate, and developed with silver, and toned with platinum. He also showed prints on uranium nitrate paper, toned (? developed) with platinum. In a subsequent paper (Journal of the Photographic Society, vol.v.p.228), Burnett recommends toning, firstly, with the nitrate, sulphate, or acetate of platinum; secondly, with a platinum toning bath rendered alkaline by the addition of any alkali or its carbonate, or by dissolving hydrated platinic oxide in a solution of one of the alkalies or their carbonates; and thirdly, neutral or alkaline baths prepared with platinous oxide or its salts. In the same article he gives a formula for an urano-nitrate paper, developed with nitrate of silver and toned with bichloride of platinum, to which has been added a solution of tartrate, acetate, or formiate of potash, until the precipitate first formed is redissolved, the solution being neutralized with carbonate of ammonia. In the Liverpool and Manchester Journal of May 15, 1858, Burnett proposed to prepare paper, either plain or collodionized or gelatinized, with ammonio-ferric oxalate, and develop it with gold or palladium, or develop with silver and tone with platinum, gold, or palladium, fixing with ammonia or oxalate of ammonia.

In the Photographic Journal of July 1, 1859, in a long paper on sensitizing and toning baths, Burnett describes the following toning baths:

1. Bichloride of platinum and carbonate of soda.
2. Platinum sulphate or nitrate.
3. The same, with a deoxidizer to reduce the plantinic to platinous salts.
4. 4 and 5 same as 2 and 3, but with platinous sulphate or nitrate.

Burnett here notes that the platinous salts are more easily reduced than the platinic ones.

Further on in the same article he describes toning baths with the chloride and nitrate of platinum, and recommends the use of the double salts that gold or platinum form with chloride of sodium, and says that the chloro-platinite of sodium should be tried. He also mentions the chloro-palladite of sodium as being a capital toning bath.

It is difficult to know exactly what merit is to be assigned to Burnett; his papers are very numerous, and it is not easy to distinguish actual experiment from mere suggestions. However, it is quite evident that in 1857 he had endeavoured to tone silver prints with platinum, and showed prints so toned in 1855. This fact give him priority over Carranza, although his paper, not having been published until 1857 he had endeavoured to tone silver prints with platinum, and showed prints so toned in 1855. This fact give him priority over Carranza, although his paper, not having been published until 1857, somewhat militates against this claim. Anyway, his uranium experiments, developed with platinum, taking the date at 1859, when they were published, although they are stated to have been produced in 1857, and shown in the same year, gives him priority over De Luynes and St. Victor. With regard to this last-named gentlemans supposed discoveries with uranium salts, Burnett carried on a very acrimonious correspondence in the different journals. Lastly, as the proposer of, if he did not actually use, the platinous salts, both for silver toning and developing prints in uranium, Burnett merits considerable kudos. It is, indeed, remarkable how near he came to discovering a really practical platinum process, namely, the Willis platinum in the bath process. Burnett used ammonio-ferric oxalate, and fixed with ammonio oxalate; and he knew that platinum salts acted as developers of paper so prepared. If only, instead of wandering off into experiments with nearly every known and unknown salt, he had stuck to and perfected this one process, it cannot be doubted but that the present platinotype process must have been forestalled by many years.

CHAPTER II.

The Salts of Iron.

It will now be abundantly clear from the above historical resume that the most practical results in platinotype are obtained by the use of iron as the chemical of which the provisional image is formed, and is replaced by the platinum according to a true chemical substitution process. We shall therefore proceed to examine the behaviour of the different salts of iron under the influence of light, borrowing largely for this purpose from the careful series of experiments that were made on this metal by Dr. Eder.*

It is known to chemists that all the ferric salts, in the presence of organic bodies, are more or less sensitive to light, being reduced to the corresponding ferrous stage; now the organic substance would of course be found in the paper itself, or in the different sizes, starch, dextrine, gelatine, etc., with which the cellulose fibre has been strengthened.

But, in choosing the most suitable salt, many conditions should as far as possible be fulfilled; first, we naturally seek the mixture which is most quickly acted on by light; secondly, the reduction of the ferric salt must not form any substance in the paper that would be deleterious to the platinum; thirdly, the salt must be more or less non- crystallizablethat is to say, it must be capable of being applied to paper in some form that will not crystallize and break up the surface in the way that nitrate of silver on a wet collodion plate, if allowed to dry, would do. Minor properties which are desirable are that some sort of a visible image should be formed on the paper to guide the printer as to the state of his print.

Dr. Eder experimented with the following of the ferric salts, and determined their rapidity of decomposition by light by measuring the amount of ferrous salt that was percipitated from their aqueous solutions in a given time. The solutions contained from one to five per cent. of ferric chloride, or a like equivalent of the particular ferric salt used, the temperature of the solutions being from 17 degrees to 20 degrees C.

Ferric chloride and oxalic acid	100
Ferric oxalate	89
Ammonio ferric oxalate	80
Ferric tartrate	80
Ammonio ferric tartrate	80
Potassio ferric oxalate	78
Ammonio ferric citrate	15
Ferric chloride and citric acid	19
Ferric Chloride and tartaric acid	25

Generally speaking, sensitiveness increases with temperature and the degree of concentration, at the same time that the differences in the quantities of ferrous salt precipitated from the solution become smaller.

For this reason he tries a fresh set of experiments, for the above mixtures, when dried into paper, might behave quite differently from the aqueous solutions under the influence of light. His method was to assimilate more closely to what would be likely to obtain when the salts were used as a basis of a positive processthat is to say, when spread and dried on paper. He therefore soaked pieces of paper in the mixtures, and exposed them when dry under one of Vogels paper photometers, simultaneously, and for an equal time. These slips were then developed with ferricyanide, when, by comparing the amount of Turnbulls blue precipitated, he was able to compare their sensitiveness. Practically no great difference was found from the results of the aqueous solutions; the ferric chloride and oxalic acid was the most sensitive; the ferric oxalate was less so; then follow the ammonio- and sodio-ferric oxalates, and the potassio-ferric oxalate was the least. The differences in sensitiveness between the double salts alone were not so great as in the case of the aqueous solutions, the sodium and ammonium salts especially being almost equally sensitive.

The rationale of the reduction of these salts Dr. Eder ascribes to the fact that with the formation of the corresponding ferrous salt carbonic acid is liberated. Dobereiner (Schweiggers Journal, vol.1xii. p. 90) first observed this decomposition of aqueous ferric solutions by light in 1831; and, later, Suckrow (On the Chemical Action of Light, 1832, p. 29), Draper (Dingles Polytechnic Journal, vol. cxlvi. p. 29), and Reynolds (British Journal of Photography, 1861, p.9). The reaction was the most regular in the case of the oxalate, as the quantity of carbonic acid given off agrees very closely with that determined theoretically; it is not so regular in the case of the citrate and tartrate, since in addition to carbonic acid, acetic and oxalic acids are also formed.

Of all the above salts of iron examined by Dr. Eder, the most sensitivethat is, the mixture of ferric chloride and oxalic acidis not serviceable in platinum printing, as in its decomposition by light hydrochloric acid is formed, and this is deleterious to the reduction of the platinum salt, and would prevent the development of the image.

Hubl and Pizzighelli made a further series of experiments on the oxalates, citrates, and tartrate, with special reference to their use in platinotype. Solutions of these salts, the degree of concentration being so arranged that after exposure there might be one molecule of platinous chloride to every two molecules of the ferrous salt, were mixed with chloroplatinite of potassium, and then applied to paper. Strips of such prepared paper were, when dry, exposed under a paper actinometer scale simultaneously for an equal time.

They were then developed with a hot solution of potassium oxalate; the result was that the paper prepared with ferric oxalate gave a much more intense black deposit, and, moreover, its sensitiveness was greater than the slips prepared with the tartrate and citrate. Further experiments with the acetate and formiate proved that the former is very little sensitive, and that the latter causes the reduction of the platinum salt very rapidly, and even without exposure to light.

As the double salts of the ferric oxalate posses the advantage of being procurable in a crystalline form, a property wanting in the simple ferric oxalate, Hubl and Pizzighelli considered it important to submit these salts to a similar examination. They could not well employ the potassium salt on account of its insufficient solubility in water, but the sodium and ammonium saltsof whose composition, especially of the amount of water of crystallization contained in them, Dr. Eders recent investigations had given them complete informationwere experimented on by these workers. They found, however, that paper so prepared was only slightly sensitive, and the images obtained inferior as regards intensity or depth of shadow, and could not compare with the results obtained by the simple ferric oxalate. They explained the unsuccess of their trials on the hypothesis that the complete reduction of the double salts under exposure is not effected with the same readiness and regularity as in the case of simple ferric oxalate; they therefore endeavoured to rectify this by reducing the quantity of the double salt in the sensitizing solution by one-half, and making up the requisite amount of iron by the addition of neutral ferric chloride.

But even with this combination they were unable to obtain reactions of any great value the intensity of the blacks was somewhat improved, but the sensitiveness was decreased, and the prints had an unpleasant yellowy-brown tone.

The upshot of the above experiments was that Pizzighelli and Hubl arrived at the conclusion that the simple ferric oxalatethe salt originally used by Williswas the most suitable for the formation of the provisional image.

Ferric oxalate is produced by dissolving ferric hydrate in oxalic acid, by which means a greeny-brown syrup is obtained; on evaporation a brown syrup is formed, which is incapable of crystallization.

Protected from light, and at temperatures of from 15 degrees to 30 degrees C., this solution will keep for months without alteration.* When heated, however, to 50 degrees C. for several hours, a gradual reduction to the ferrous oxalate takes place, and this reduction will be effected much more quickly if the solution or paper coated with it is exposed to the action of light. The ferrous oxalate thus formed consists of a light yellow crystalline powder, soluble with difficulty (1 part in 1000 H20 at 15 degrees C.), but which is stable under the action of light or air, even when in a moist condition.

Dr Eder found that this salt, when moistened with solutions of the alkaline oxalate, had a very powerful reducing action, and, according to Pizzighelli, solutions of the alkaline acetates, benzoates, succinates, borates, and phosphates, as well as the solutions of the alkalis and of the alkaline carbonates, produced the same effect. They ascribe the reaction to the formation of either soluble double salts, or insoluble ferrous salts, having energetic reducing effects. With the caustic alkalis, and especially with the alkaline carbonates, ferrous oxide itself is probably formed, a well- known reduction agent.

The Action of the Spectrum on the Salts of Iron.

Dr. Eder, to whom we are largely indebted already for his researches on the behaviour of the iron salts under the action of light, has also published an interesting account of their behaviour in different parts of the spectrum.*

From these experiments we cull the following results, which may be found useful in examining the general behaviour of platinotype processes.

Ferrous Salts.

Ferrous, as well as ferric salts, are reducible both by light and heat. In the dark, however, ferrous sulphate oxidizes less rapidly than when in contact with air and red light, and the purely chemical action, when shaded from light, is greater than oxidation in presence of violet light. According to Chastang the oxidation is as follows:

In darkness	1.00
Red light	1.46
Violet light	31
Green Light	80

The oxide formed was ascertained volumetrically.

Ferric Salts.

A solution of ferric chloride in ether passes into the ferrous state when exposed behind blue or white glass, and not behind yellow or red (A. Vogel). According to Chastang the violet rays are those which reduce solutions of ferric chloride in ether to the ferrous chloride with the greatest rapidity. In the dark or in yellow or red light a little ferric oxide separates. Dobereiner found that an aqueous solution of ferric oxalate was decomposed into carbonic acid and ferrous oxalate by sun light and by blue and violet light, but not by red or yellow (Schweiggers Journal, vol.lxii. p. 92).

Suckow found that the action of light on ferric oxalate, after passing through a violet glass, was the same as that of white light; the action was retarded by a blue glass, and still more by a green. In yellow or red light he remarked no change.

Reynolds (British Journal of Photography, 1861, p. 9) compares the relative action of the solar spectrum on paper impregnated with ferric oxalate, and that prepared with silver chloride. He found that the action of light was nearly the same.

According to Eder, ferric oxalate is relatively more sensitive to the green than silver chloride. A mixture of ferric chloride and oxalic acid, or of oxalate, behaved in the same way. It was also the same when double oxalates of iron (ferricum) and ammonium, or potassium were used.

Actinometers, in which ferric oxalate is used as a basis, give, according to Eder, a measure of the ultra violet, blue, and blue-green rays, the same results being obtained when ferric chloride and oxalic acid are used.*

Marchand (Etude sur la Force Chimique, 1875) examined the action of the spectrum on a mixture of ferric chloride and oxalic acid, with which he had filled his photometer. He measured the action of the different rays by the quantities of carbonic acid eliminated during equal exposures. His results were as follows:

In the Red rays	5.7
Orange	9.9
Yellow	43.1
Green	134.1
Blue	615.8
Indigo	370.0
Violet	321.0
Ultra-Violet	52.1

The work of Marchand showed (lst) that oxalic acid allowed all the rays to pass; (2nd) that ferric chloride only allowed the red, orange, yellow, and green, and a very little blue; (3rd) that a mixture of the two only allows the red, orange, yellow, and green to pass, without a trace of the blue. Marchand measured the intensity of the luminous action by a quantitative determination of the ferrous oxide produced, or by the quantity of carbonic anhydride disengaged during oxidation of the oxalic acid. It should, however, be stated that Becquerel contests the accuracy of the above results of Marchand, who defends his method against the formers criticism by saying that he did not wish to determine the chemical intensity of the light, except so far as it had acted on the liquid (Ann. Chem. Phys. (5) vol.ii. p. 160). As Eder also points out, in this method, the absorption of the carbonic acid by the liquid must be taken into account, this absorption varying with temperature and pressure, besides which, for small quantities, the process would be liable to give inaccurate results.

Draper noticed that the ammonio-citrate of iron (ferricum) brushed on paper is reduced as far as the blue-green to near F. Herschel remarks that a mixture of this salt and potassium ferricyanide rapidly becomes blue in the blue, in the violet, and ultra-violet, the blue rays having the maximum effect. A mixture of ferric chloride and tartaric acid exposed to white light and to coloured light in the same manner as the organic salts of iron already described, is less sensitive, according to Eder, than the oxalate.

Ferric sulphocyanide in aqueous alcoholic or etheric solution, which is of a beautiful red colour, is reduced, according to Grottus, principally by the blue-green rays.

Herschel (Hunts Photography, 1852, 3rd Ed. p. 56) gives some interesting experiments on the behaviour of some iron salts under the influence of heatthat is to say, the lower rays of the spectrum. Paper was washed with ammonio-citrate of iron and potassium ferrocyanide in about equal proportions; it was exposed to sunshine, washed, and dried. He then washed this paper with mercurous nitrate, and on exposing to a concentrated spectrum its whiteness was changed to brown over the whole region of the red and orange rays, but not beyond the luminous spectrum.

Sir John also proceeds to show that the reduction of the iron salts is chiefly by the blue rays. A slip of paper prepared with ammonio-citrate of iron was exposed partially to sunshine and washed with bichromate of potash; the bichromate is deoxidized and precipitated upon the sunned portion, just as it would be if directly exposed to the suns rays. In a subsequent chapter will be found a fuller account of the experiments which we have made.

CHAPTER III.

The Salts of Platinum.

Our readers may have remarked that, in early platinum processes of Carranza, platinic chloride was used, this salt being variously known as bichloride of platinum of the old chemistry, or tetrachloride of the new: whereas, with the processes of Willis, the double chloro-platinite of potassium is used. In order to solve the question whether this was the best salt for the purpose, Pizzighelli and Hubl went through a variety of experiments, which we describe literatim from their book.*

In the process now before us the salts of platinum play a much more important part than those of iron, as from them is derived the metal of which the image is finally composed. As already stated, in the production of this image the salts are reduced; hence only those salts of platinum are suitable which are capable of being readily reduced by the above-mentioned reducing agents, and which for this purpose require the use of comparatively small quantities of the ferrous salts. Further, as in sensitizing the paper the salt of platinum is applied simultaneously with that of iron, all those compounds of platinum are excluded from consideration which, is mixing with the salts of iron, may give rise to disturbing reactions. Of all the salts of platinum, the chloride, bromide, and iodide seem best to fulfil the first of these conditions; while the sulphite, the double-cyanide compounds, and the double salts of ammonium and platinum are either not reduced at all, or are reduced with very great difficulty. Independently of this, however, the first-named salts are to be preferred, on the ground that they can be prepared more easily, and are therefore cheaper.

The chemical reaction in the formation of the image is, according to Berkeley (Photographic News, 1882, p. 157), most simply represented by the following equation;

For platinous chloride

Ferrous Platinous Ferric Ferric

oxalate chloride oxalate chloride Platinum

$12FeC204 + 3PtCl2 = 2Fe2(C204)3 + Fe2Cl6 + 3Pt$

Analogous is that for platinic chloride

Ferrous Platinic Ferric Ferric

oxalate chloride oxalate chloride Platinum

$12FeC204 + 3PtCl4 = 4Fe2(C2O4)3 + Fe2Cl6 + 3Pt$

The correctness of these equations is, however, rendered doubtful by our observation of the formation of gas when the image is developed in a hot solution of potassic oxalate. Now, this reaction can only be due to the fact that the remainder of the oxalic acid, combined with the iron, is displaced by chlorine, and separates as carbonic acid in a gaseous form. We may therefore assume that the reaction is not quite so simple as the equations would indicate, but is probably much more complicated. It should also be borne in mind that the platinum salt itself, as we have already had occasion to mention, undergoes a slight alteration under exposure to the light.

But whatever the real process of reduction may be, it is clear that the platinic chloride requires just twice as much ferrous oxalate for its complete reduction as the platinous chloride. This explains why it is scarcely a matter of no importance whether, with Willis, we employ for developing the image a platinous salt, or, with Koninck and Roppe, a platinic salt. The quantity of ferrous salt need not be so large in the first case as in the second; and as the ferrous oxalate is only formed by exposure, the duration of that exposure may be considerably less when a platinous salt is used than is required in the case of a platinic salt.

As in every other photographic printing process, we find also in this that the more sensitive substance gives soft pictures with a hard negative, and with a soft negative weak pictures, while the substance requiring a longer exposure will give, in the one case a hard, in the other a brilliant, picture. It will, therefore, be more advisable to employ generally a platinous salt as a sensitizer, and to mix with it, when the negative is soft, a little of the corresponding platinic salt, or, when the negative is weak, a larger quantity of the latter.

According to our own experience, of all the platinous salts, the platinous chloride and the double salts of platinous bromide best comply with all the required conditions, and of the latter the platinous bromide of potassium is to be preferred. The double salts of platinous iodide cannot be used, as in mixing with the ferric oxalate salt they reduce it, with separation of iodine. The corresponding simple saltsthat is to say, the platinous chloride and bromide are insoluble in water; before they can be used, therefore, they must be dissolved in solution of the corresponding haloid acida process which, as has already been explained, cannot be carried out on account of the free acid present.

Potassium chloro-platinite and the corresponding bromoplatinite posses the advantage of being easily prepared and purified; but, on the other hand, the disadvantage that they cannot be mixed with platinic chloride and its double salts without the formation of an insoluble precipitate of potassium chloro-platinate. This defect is not found to exist in the case of sodium, lithium, and magnesium double salts; but the first two crystallize only with difficulty, and it is on that account troublesome and costly to obtain them pure. Besides, they are hygroscopic and deliquescent in a high degree; and as the quantity of water they contain is so variable, they cannot be accurately weighed without special arrangements and precautions. The magnesium salt is not deliquescent; but it does not readily crystallize, and cannot, therefore, be easily obtained in a pure state. The calcium, barium, and strontium salts cannot be used, from the fact of their forming insoluble precipitates with ferric oxalate.

A consideration of the comparative advantages and disadvantages possessed by the above-mentioned platinum compounds, leads us to give the preference to the potassic salts; and, as the preparation of the potassium bromo-platinite is much more troublesome than that of the corresponding chloro-platinite, we determined to carry on our experiments with potassium chloro-platinite. We desire, however, to draw attention to the circumstance that, according to our experiment, the double salts of potassium, sodium, lithium, and magnesium all five identical results in the production of the image, both as regards their reducing powers and as regards the appearance of the finished picture.

When preparing a sensitizing solution of chloro-platinite of potassium, adapted to the character of the negative from which the copy was to be taken, we were compelled to leave out of the question the direct addition of a platinic salt, partly because a mixture with the double salt of platinic chloride is not feasible, and partly on account of the difficulty and expense of preparing a more suitable platinic salt. But we tried whether the required advantage could not be obtained by adding the oxidizing substances, which have not the effect of immediately decomposing the sensitizing solution, but only convert more or less of the platinous into the corresponding platinic salt at the time when the solution dries up on the support.

The Substances Suitable for the Development of the Platinum Image.

If paper coated with ferric oxalate and chloro-platinite of potassium, or ferric oxalate alone, be exposed to light, and then treated with hot or cold water, or in the second case treated with chloro-platinite of potassium or platinum tetrachloride in water, no image, further than the already existing one formed directly by the action of light, will be formed. As a matter of fact, the ferrous oxalate in presence of moisture has a slight reducing action, but it is so slight that the image will be dissolved out by the water before it is formed.

In this respect the action of the iron salts is different to that of the silver ones, for there, as we see in Carranzas process with platinum tetrachloride, or Clarks with platinum chloro-platinite, nothing more than an aqueous solution of these salts is necessary to bring out a strong platinum image.

Willis, in his hot-bath process, floats the paper over a hot solution of oxalate of potash, or, in his cold-bath process, with oxalate of potash and disodic orthophosophate. Besides the oxalate of potash, there are many substances that are capable of acting as developers; some act best when applied hot, or some cold; they will even act, in the presence of moisture, when they are contained in the coating ingredients of the paper itself, as in Pizzighellis new process.

These developers, as they are usually called, have been carefully investigated by Pizzighelli and Hubl, and we give the results of their experiments.

Developers are used both in the hot and cold bath processes; in the former they act really like a gelatine plate developerthat is to say, they in no way go to make up the structure of which the image is built, but simply act as a vehicle or conveyance between the provisional and resultant image. In the cold-bath process, however, the developers themselves contain the platinum salt or colouring matter. It will be, therefore, readily understood that a different set of chemicals may be required for the one process from those used with others. We shall, therefore, commence by treating of those used with the old or hot-bath process.

Although this process is always known as a hot process, it does not by any means follow that cold developers cannot also be used in it; in fact, when we come to the practical details of the process, we shall see that certain advantages are gained by using the solution cold. In the following list of developers, which are given in the order of their reducing power, they are, with the exception of Nos. 11, 12, and 15, applied in solutions at a temperature of 80 degrees C., the solution, when not otherwise specified, being concentrated.

The experiments were carried out by exposing strips of paper under a graduated scale to the same light, for the same time, and comparing the results obtained both as regards the number of gradations brought out-that is, the rapidityand also the opacity or quantity of platinum salt reduced.

1. Sodium acetate: very energetic, giving soft pictures with a yellow tinge, owing to formation of basic ferric acetate, but can be discharged by subsequent treatment with hydrochloric acid, or minimized by strongly acidulating the developer with oxalic or citric acids.
2. Sodium acetate and oxalic acid: acts same as No. 1, but give pure whites.
3. Potassium citrate: behaves most identically with 2.
4. Sodium carbonate (hot): acts much the same as the above, but forms yellow-coloured basic-ferric salts; an insoluble precipitate is also formed in the developing bath.
5. Ammonium citrate (neutral) give the same result as above, but without basic precipitate.
6. Ammonium citrate (acid) as used for developing chloride of silver pictures: same results as No.5.
7. Potassium oxalate: ditto.
8. Rochelle salt: ditto.
9. Ammonium benzoate: same as No. 4. 10. Sodium succinate: ditto
10. Caustic potash (cold, sol. 1 in 25): much inferior in power to the above.
11. Sodium carbonate (cold): ditto.
12. Sodium phosphate (cold): ditto.
13. Water (hot)
14. Ammonia possess only a moderate power of *

15. Oxalic acid developing

The different citrates are practically too expensive, and give no compensating greater advantages over the rest, and are therefore out of the field. All the latter developers from Nos. 11 to 16 are too weak in their action to be of any use. Of the remaining mixtures, the sodium acetate, potassium oxalate, and Rochelle salt are the best, but Hubl and Pizzighelli give preference to the potassium oxalate, and as this salt is the one that is recommended by Willis in his practical working instructions of the process, it may be fairly assumed that it is the best.

The Effect of the Presence of Foreign Bodies in the Sensitizing or Developing Solutions.

It is hardly necessary to point out that it is always a necessity to keep the different ingredients used in all sorts of platinotype processes absolutely free from foreign bodies, and also, to ensure the best results, that chemicals of the most absolute purity should be obtained. There are many substances that act, even when present in small quantities, very vigorously on the platinotype image; in fact, the mere difference between alkalinity and acidity, whether of the sensitizing or developing mixtures, produces decided differences in the result.

Generally speaking, the sensitizing solution should have an acid reaction in order to prevent the formation of any insoluble basic iron salts, which give to what should be the whites of the picture an unpleasant yellowish tinge, which often is not removed by hydrochloric or other acids; but, at the same time, excess of acid is also to be avoided, as this hinders the substitution of the iron and platinum in the development.

With regard to the state of the developer, Pizzighelli recommends that this should be kept distinctly acid; but the Platinotype Company, in their instructions, lay special stress on the fact that on no account should any acid be allowed to get into the developer, which should be kept distinctly neutral. We must confess that we entirely agree with the Company, and consider that the solution should be kept neutral. The presence of any acid in the developer is apt to cause granularity in the print. When a hot development is used, there is but little time for this to show, but if the development be effected with tepid or cold solutions, when the process naturally takes much longer, this is sure to make itself evident. Its cause is probably to be found in the fact that the acid bath is capable of dissolving out, or rather commencing to dissolve out, the provisional iron image before this has had time to reduce the platinum salt. We have even found it advantageous to render the bath, when the development is effected with an absolutely cold (60 degree F.) solution, distinctly alkaline with ammonia. In this case, no insoluble basic iron salt appears to be formed in the paper. On the addition of the ammonia to an old bath containing iron, a precipitate is at once formed, which, however is redissolved by the same bath almost immediately. We therefore recommend that with hot development the bath be kept neutral, and with cold development rendered slightly alkaline with ammonia.

In using the term acid as applied to the sensitizing solution, it must be remembered that ferric oxalate, like many other of the acid iron salts, gives an acid reaction in itself when pure, and, therefore, considering it as a neutral is not strictly correct. At the same time, acids may be found present in carelessly prepared chloro-platinite of potassium, and as the presence of any mineral acid is highly injurious to the formation of the image, the salt, if purchased, should be carefully tested for a neutral reaction. At the same time, acids may be found present in carelessly prepared chloro-platinite of potassium, and as the presence of any mineral acid is highly injurious to the formation of the image, the salt, if purchased, should be carefully tested for a neutral reaction. At the same time, Pizzighelli recommends the addition of 6 or 8 per cent. of oxalic acid in the sensitizing solution, and the addition of an inorganic acid does not appear to affect the ultimate result.

Pizzighelli states that the presence or absence of acid affects the colour-tone of the pictures, a neutral sensitizer giving a brownish picture, and an acid one a bluish picture. These results would therefore agree with the observations of Gwenthlian, but we cannot, however, agree with either of these authorities, at least as regards the toning of silver prints; here the presence of alkalis or acids has no action on the resulting colour. The only thing, besides of course the addition of other chemicals, that affects the colour-tone is, in our experience, the composition of the sizing of the paper. It is, of course, possible that the acid in the sensitizing solution may tend to destroy some of the sizing in the platinotype paper, and so cause the phenomenon that Pizzighelli describes; we ourselves have, however, never met with it.

Reducing Substances.

The presence of any of thesewith the commoner ones, such as hyposulphite of soda (sodium thiosulphate), formic acid, sulphurous acid, chromic acidshould be carefully avoided; they tend both to reduce the ferric oxalate and the platinum and therefore cause fogging in the high lights. Their presence appears to be injudicious, even when in the smallest proportion.

Oxidizing Substances.

The action of these substances is, of course, directly the opposite to the above; they tend to undo the action of light, reconverting the ferrous salt formed by the agency back again to the ferric stage. They have also probably an action on the platinum salt itself, converting this also from a platinous into a platinic salt, the precise chemical form it takes being probably the insoluble potassium chloro-platinate.

When any platinic salt is present, it requires twice as much ferrous salt to replace it as does the platinous salt. Since the quantity of the platinic salt is, by the addition of an oxidizer, equally formed over the whole surface, whereas the ferrous oxalate, or the reducer, is formed only by the action of light, it follows that in the high lights, where the formation of ferrous oxalate is very slight, the platinic salt is relatively largely present; but in the deep shadow, where the ferrous salt is plentifully formed, the amount of platinum remains constant, and is relatively a small part of the whole. Therefore, on development, the presence of the platinic salt is but slight in the shadows, but relatively great in the high lights, and the print gains in brilliancy, or if the platinic salt be present in large excess, positive hardness my result.

But any oxidizing chemical in any proportion can be practically used for this purpose, provided they do not form chloro-platinate in the mixture, which, once formed, could not be evenly applied to the paper. It is therefore generally accepted that chlorate of potash is the best oxidizing substance to use; it appears to be almost without effect on the solution, only acting when this is dry. The explanation of this is that the first action of the chlorate of potash on the iron salt is the formation of ferric chlorate; the salt is, however, unstable, and gradually, during drying, hands over its oxygen to the potassium chloro- platinite. The action of chlorate of potash is, however, very energetic, and it must be added with great care and scrupulous exactitude. The presence of such a minute quantity as one-hundredth per cent. is said to make itself evident.

If the sodio-chloro-platinite be used instead of the potassium salt, in that case, sodium-chloro-platinate can be directly added instead of chlorate of potash.

Very great power is in the hands of any person who prepares his own paper; by a suitable proportion of this salt a perfect gamut of results from softness to hardness can be obtained, and the paper prepared to suit the character of the negative to be printed from.

CHAPTER IV

Preparation Of Paper For The Hot-bath Process.

Part I.

Choice of the Paper or Support.

Almost any quality of paper, providing it be free from metallic or other impurities, can be used for platinotype. At the same time, the acid bath to which the print has to be subsequently treated has a great tendency to rot the texture of the paper, making it easily torn in the subsequent handlings. It is, therefore, advisable to choose a somewhat heavier paper than the ordinary brands of Rive and Saxe, used for silver printing.

The state of the initial sizing of the paper has an important influence on the resulting print. The sensitizing solution in platinotype might almost be considered to be in the form of an emulsion, and is smeared or spread over the surface of the paper, and it is, therefore, necessary to keep the solution as much on the surface of the paper as possible. If a paper almost unsizedsay, such as plate paperwere used, it should be treated to a supplementary sizing before the sensitizing solution is applied, or it will all sink into the body of the paper, and give weak and flat images. At the same time, the majority of papers that one is likely to experiment with are already sized sufficiently to dispense with the preliminary coating, but some gelatine or arrowroot must be added to the sensitizing solution, or the platinum black will wash off.

More mistakes are apt to happen in the correct sizing of the paper than in any other portion of the manipulation, different brands of paper requiring different treatment. The point to aim at is to sufficiently close the pores of the paper, to prevent the sensitizing solution sinking in, but at the same time to leave them sufficiently open to enable the platinum to attach itself to the paper, and not fall off into the developing bath.

The Platinotype Company themselves sell one or two different marks of paper, particularly suitable for the preparation of platinotypes. These papers are probable resin-or arrowroot-sized, these substances having certain advantages over gelatine, which is coagulated by the salts of platinum, and is apt to work in streaks. Pizzighelli recommends a paper made by Gustav Roder and Co., of No. 10, Wallfischgasse, Vienna, at their mills at Marchendorf, called ivory vellum, which may be obtained either hot pressed or not. Rough paper, such as Whatmans rough drawing-papers, are not very suitable for platinotype; there is a great difficulty in spreading the solution on them, as it has a tendency to be brushed off the tops of the granules into the valleys, causing the print to turn out very rough, granular, and uneven.*

Perhaps the best procedure to follow in such a case is to apply a ten or twenty per cent. solution of dextrine to the paper before sensitizing it. This forms a temporary coating, and keeps the sensitizing solution on the surface, but gives no hard or shiny appearance to the paper, as it is largely removed in the subsequent washings.

Part II.

Preparation of the Paper.

For an average paper, such as a heavy Saxe or Rive, or a Whatmans No. 1, the following is the proportion of the sizing solution it is advisable to apply:

Gelatine (any good brand will do, such as Nelsons coating gelatine) 10 grains.

Water 2 ounces.

The gelatine is allowed to soak thoroughly till swollen; it is then dissolved by gentle heating, and 3 grains of powdered alum are added and ½ ounce of methylated alcohol. It should be filtered hot through a jelly bag or canvas, taking care that no bubbles are formed. The above solution should hardly solidify at 70 degrees F.

Arrowroot.The same amount is to be used, the flour being first rubbed up with a little water till it forms a stiff paste, and 2 ounces of hot water are added with careful stirring, and brought up to the boiling point, when the arrowroot will lose its milky colour, and become transparent and gelatinous in its consistency; ½ ounce of alcohol is added, and, after straining, the size is ready for use.

Either of the above sizes are applied by immersing the sheets bodily in the solution spread out in a flat dish. A little care is necessary in this operation to avoid air-bells, the best way being to plunge the piece of paper into the solution, beginning at one edge, then turn it over, and with a glass triangle break any bubbles that may form. After a couple of minutes immersion, it should be drawn out slowly and steadily without making any stoppage; in this manner the superfluous liquid will be left in the dish, and not be carried off on the surface of the paper. The paper should be hung up to dry in a warm room, or before a stove; if the room be too cold, the gelatine will be found to set in a line along the bottom of the paper, instead of dripping off as it should do. In any way, as the gelatine or arrowroot will have naturally gravitated down to the lower endwhich will be, therefore, more highly sized than the topit is advisable to repeat the above operation, reversing the paper end for end during the drying.

Heavy papers should not be immersed in the solution, it being quite sufficient if they be simply floated, and left for a minute or two on it; it is still advisable, however, to size them twice, reversing the position in which they are dried.

Although not so successful in its results, still it is practicable to simply brush the sizing on the surface of the paper, and to let it dry; this method will be found useful where it is required to only sensitize a single sheet of paper.

Another very excellent way of dealing with the finest sorts of stuffs or paperssuch as sarsenet, or the Japanese rice papers, or India papersis to first mount them bodily on a thicker paper by means of dextrine, and in this condition to sensitize, print, and complete all the operations. The picture, when finished, can be removed from its mount by warm water, in which the dextrine is of course soluble. In this manner the very flimsiest of materials can be successively handled.

Preparation of other Supports.

Linen and other Fabrics.The procedure to follow with these materials does not essentially differ from that when paper is used. A little care has to be taken with these stuffs, to see that they do not crease or dry in stiff folds from the action of the size. They should, whilst still wet from the second sizing, be stretched on light wooden frames, in which state they will dry perfectly flat; the sensitizing liquid can also be most conveniently applied to them whilst they are still stretched on their frames.

Preparation of Wood.

Soft and Hard Woods.The surface of wood to receive the sensitizer must be carefully and evenly smoothed. If the wood has to be impressed with a picture for merely ornamental purposes, the above sizing solution can be applied to it, and then be allowed to dry; a little care may be necessary to prevent the wood warping, and as soon as the surface moisture has evaporated, it should be placed under pressure, when it will be found to dry straight.

If the wood is to form a basis for the gravers tools, it is important to moisten it as little as possible, as any damp rots the fibres, and makes the cutting of the fine lines very difficult. No sizing solution should be used, but the sensitizer, having as little moisture in it as possible, must be rubbed well into the block till dry. For the purpose in question it is not removed to get an even surface, nor is the same vigour necessary, and no difficulty should be found in preparing boxwood blocks. The cold development is more suitable for the purpose than the hot; in fact, to use an Irishism, the hot bath should be worked cold, the surface being merely moistened with the cold oxalate solution.

(Although the above instructions may be useful to persons abroad, or who wish to prepare some special kind of paper fabric, or substance for platinotype printing, it must not be forgotten that suitable sized papers (special qualities, hot-pressed, not rough, and also different sorts of fabrics), can be obtained from the Platinotype Company, all ready sized; in this state they are, of course, practically unalterable, and can be sent without danger to any part of the world.)

Part III.

Preparation of the Sensitizing Solution.

Hitherto we have been dealing with ordinary mixtures that are entirely unaffected by light, and all the previous operations can very well be carried out, even in sunshine, and the simply sized paper can, of course, be prepared and stored away in any quantity, and is practically unaltered by time. But the operation of sensitizing must be performed in a suitable lighted or rather darkened apartment. The sensitizing solution is decidedly more active to the feeble rays of light than is ordinary silver paper, and as no change is visible shown of the first commencement of reduction, it is advisable by a few trials to assure ones self of the safety of the coating room. Yellow light is unsuitable for coating the paper, owing to the colour of the sensitizing mixture being the same, it thus being difficult to distinguish the coated from the uncoated parts, and streaks may result. A really good paraffin lamp will, however, give a light nearly white enough, although weak daylight filtered through white tissue paper is preferable. In all cases the paper should be exposed as little as possible, and during the drying should be carefully protected from all white light.

The preparation with which the paper is coated, consists of a mixture of chloro-platinite of potassium and ferric oxalate, to which may be added, to obtain certain effects, chlorate of potash. The chloro-platinite of potassium, the making of which requires a good laboratory, and some chemical knowledge, should be preferably bought ready prepared, it being now obtainable from all large chemists and photographic dealers. In the Appendix we give, however, full directions for its manufacture from metallic platinum.

The ferric-oxalate solution, even if bought from the chemist, demands a certain amount of quantitative analysis, as otherwise it is impossible to estimate its strength; we therefore give here in full, Messrs. Pizzighelli and Hubls method of manufacturing and estimating this.

Preparation of the Ferric-Oxalate Solution.

For the preparation of the solution of ferric oxalate the following operations are necessary:(1) Manufacturing the ferric-hydrate; (2) dissolving the substance in oxalic acid; (3) determining the amount of iron and of oxalic acid contained in this solution; (4) diluting and acidulating the same.

The method of preparing ferric hydrate is generally well known, but, for the sake of completeness, we will give a brief description of it. Five hundred grams of ferric chloride are dissolved in from five to six litres of water, and, when the solution has been brought to the boiling point, a solution of soda is added until it gives with litmus paper a distinctly alkaline reaction. For this purpose about 250 grams of caustic soda will be found necessary. The precipitate is then washed with hot water by decantation until the wash-water is no longer alkaline. It is next placed in a cloth, and, by pressure, freed from the greater part of the water. With the ferric Hydrate thus obtained, which ought to have a syrupy consistency, there should be mixed about 200 grams of finely crystallized oxalic acid, and the mixture be then left to itself for a few days at a temperature of not more than 30 degrees C., and in a place completely protected from the light; under these circumstances the formation of ferric oxalate will go on steadily. Some persons recommend the promotion of this process by digesting the mixture for some time at a high temperature; this we are decidedly opposed to, since, by heating for even a few hours to 50 degrees or 60 degrees C., the salt will be partially reduced to ferrous oxalate. At the commencement the solution has a pure green colour; by continued cooking it turns yellowish-green, and finally greenish-brown. When this moment has arrived, the remaining ferric hydrate should be filtered off, and the solution be submitted to quantitative chemical analysis.*

Although the determination of the amount of iron and oxalic acid contained in the solution is one of the simplest of analytical operations, we tried at first to dispense with it. Closer investigation, however, proved to us how necessary it is to confine the relations between rather narrow limits, in order to ensure the success of the platino-ferric process. Now, as ferric oxalate cannot be prepared in a stable form, so as to have a constant composition, there remains no other way than that of determining the composition of the solution by analysis, and then diluting it to the required degree. Further, it should be noted that any quantity of the solution my be prepared at once, and then kept in stock.

From the analysis we ascertain the quantity of ferric oxalate contained in 100 c.cm. of the solution, as well as any slight excess of oxalic acid which happens to be present. The liquid is then diluted with so much distilled water that every 100 c.cm. of it may contain 20 grams of ferric oxalate ($Fe2(C2O4)3)$). Crystallized oxalic acid is then added until, with the free acid already in the mixture, that substance amounts to from 6 to 8 per cent. of the ferric oxalate already in the solutionthe normal ferric solution.

An iron solution purchased from the chemist must be tested in the following manner before it is used:It must not turn blue with a solution of ferricyanide of potassium (red prussiate of potash). When boiled and diluted with ten times its quantity of water, it must not become turbid. From the first reaction we ascertain the absence of ferrous salts; from the second, that of basic ferric oxalate.

In order to introduce into the sensitizing solution some chlorate of potash, which in certain circumstances is necessary, the best way is to keep ready for use a mixture of chlorate and ferric solutions. It can be prepared by measuring off a certain quantity of the normal ferric solutions, and mixing with it so much chlorate of potash as to cause 100 c.cm. of the liquid to contain 0.4 gram of the salt. This is normal chlorate of iron solution.

Both the ferric solutions must be kept away from light.

Another method of preparing ferric oxalate is given by Weissenberger (Phot. Mittheilungen, No. 400; and Bull. Belg de Photo., vi., N.S., p. 960). Dissolve 40 grams of anhydrous ferric sulphate in 400 c.cm. of hot water, then add 86 drams of pure crystallized sodium carbonate dissolved in 200 c.cm. of hot water. A precipitate is thrown down, and this is to be washed until the last water gives a neutral reaction to litmus. 49 grams of powdered oxalic acid have then to be added to the precipitate, which should all dissolve with evolution of carbonic acid gas. When ebullition has ceased, and all precipitate is dissolved, make up the bulk with water to 187 c.cm. This solution should then contain 20 per cent. of ferric oxalate and 6 per cent/ of free oxalic acid. (We might mention that we do not quite understand how Mr. Weissenberger succeeds in dissolving his ferric sulphate in the quantity of water given.)

The Sensitizing Solution.

The precise proportions of the substances composing this depend somewhat on the effect wished forthat is to say, whether a hard or a soft print is to be obtained.

We have the following stock solutions: POne part by weight of chloro-platinite of potassium is dissolved in six parts of distilled water, and labelled stock solution. A and Bthe ferric oxalate and the mixed ferric oxalate and the mixed ferric oxalate and chlorate of potash solution (described in previous page). The standard size for platinotype paper is 26 by 20 inches, or, in French measures, 50 cm. by 66 cm., and such a surface should require about 10 cubic centimetres or grams of solution (the amount is equivalent to 154 fluid grains, or 168 minims).

This is the quantity given by Pizzighelli. The Platinotype Company, on the other hand, put down 140 minims as being the average quantity.This discrepancy is easily explained by the different texture of the paper used. It is clear that certain papers must require more than others, and, therefore, these amounts are merely indications.

For soft results, but with rich blacks:

P or Platinum solution	24 c.cm.	or 6 drams.
A or Ferric-oxalate	22 c.cm	or 5 ½ drams.
Water	4 c.cm	or 1 dram.

Distilled water quite free from lime or iron must be used.

To get greater brilliancy, use:

P or Platinum solution	24 c.cm.	or 6 drams.
A or Ferric-oxalate	18c.cm	or 4 ½ drams.
B or Ferric-chlorate	4 c.cm	or 1 dram.
Water	4 c.cm	or 1dram

To obtain results corresponding to silver images:

P or Platinum solution	24 c.cm.	or 6 drams.
A or Ferric-oxalate	14 c.cm	or 3 ½ drams.
B or Ferric-chlorate	8 c.cm.	or 2 drams.
Water	4 c.cm	or 1 dram.

For very weak negatives:

P or Platinum solution	24 c.cm.	or 6 drams.
A or Ferric-chlorate	22 c.cm	or 5 ½ drams.
Water	4 c.cm	or 1 dram.

The lessening of the amount of platinum present, or rather its replacement by water, will have the effect of giving very soft prints with no blacks, resembling pencil drawings, and, as such, are most suitable for being subsequently coloured.

On highly sized and hard papers the small amount of water may be totally omitted.

Platinotype Companys Instructions.

The above proportions are those given in Pizzighelli and Hubls work on Platinotype, but, for the convenience of purchasers residing abroad, the Platinotype Company prepare special solutions for coating their paper or prepared fabrics. The ferric oxalate is sold in two solutions, known respectively as Iron Solution A and Iron Solution B. By varying the proportion of these, harder or softer effects may be obtained. The following are recommended:

For good half-tone, suitable for brilliant negatives, with strong contrasts:

Iron Solution A	1 part.
Iron Solution B	7 parts.

For a harder effect, suitable for thin weak negatives:

Iron Solution A	1 part.
Iron SolutionB	3 parts.

By increasing the proportion of A, a tendency to hardness or destruction of half-tone is obtained. By increasing the proportion of B, on the contrary, a tendency to produce flatness, or all half-tone, is given. If A is present in quantities of less than one-eighth, there will be a tendency to get stained or fogged whites.

To the above solutions, of whatever proportion made up, there is added chloro-platinite of potassium in the proportion of 1 dram (60 grains) to each fluid ounce, or 1 in 7.3.

A comparison of the quantity of platinum used in this and Pizzighellis formula is interesting.

Pizzighelli gives, in 50 parts of solution, 24 parts of platinum solution of 1 in 6that is equivalent, then, to 4 parts of the salt in 50, or 1 in 12 ½; whilst the Platinotype Company recommend a strength of 1 in 7 1/3, or nearly twice as much. It must be remembered that, whereas Pizzighellis amounts were chiefly adduced from theory, Willis has had a much larger experience, and there is no doubt that by increasing the quantity of platinum the tendency is to give better images, more visible is the printing-frame, and of richer colours.

It must be borne in mind, however, that the above solutions, however mixed, will not keep long, and, therefore, only the quantity likely to be required should be made up. The solution will only keep in hot weather about ten minutes, or in cold weather perhaps twice as long.

Part IV.

Coating the Paper.

The operation of coating the paper may be shortly described by saying that the paper is laid down flat, the measured amount of sensitizing solution is then poured on, and brushed equally over the surface; the paper is then dried.

It is evident that these manipulations may be carried on in several ways, and any one used to coating such surfaces may proceed in his usual manner. For those who have no experience, the following hints may be found useful.

To keep the Paper Flat during Coating.

Pizzighelli recommends the following system. The paper is laid down on a sheet of glass about the same size as itself, but whose corners have been cut off. The corners of the paper are then nipped by wooden American clips. These clips are attached by indiarubber bands to pins on a drawingboard or other support of larger dimensions than the glass sheet. In this manner the clips holding the paper always tend to stretch it equally away from the centre, and, although the paper expands, it still retains its flat position.

A slightly different plan has also been suggestedvery suitable where smaller pieces of paper are coatedand that is to clip the top of the sheet of paper laid out on a sheet of glass by a wooden or glass toggle clip. Such a clip is instantly constructed by the aid of an indiarubber band.

Fig.1.

The glass clip is, of course, made the full width of the paper to be coated, and, therefore, holds the whole of one end of the sheet firmly. The left hand is then used to hold the bottom of the sheet extended, whilst the right hand does the coating. If it be preferred, the two systems can be combined, and, whilst the top end of the sheet is held by one broad clip, the two bottom ends can be extended by the elastic American clips.

Beginners will do well to commence by coating small sizes of paper, say, 13 by 10that is, the quarter of the whole sheet of platinotype paper, 26 by 20 (half double elephant). Such pieces can be conveniently coated by doubling half an inch at each end under a piece of 12 by 10 glass, and so held securely.

The Pad.

It is important that no pressure be exerted on the surface of the paper, or its texture may become abraded when, the sizing being removed, the sensitizing salt will sink more deeply into the paper at this spot, and cause a degradation of vigour in the subsequent image. The pad should therefore always be made of some yielding material, such as pure cotton-wool, or swansdown calico, or good flannel, and all hard or projecting surface be guarded against. Many ways will at once suggest themselves: a light roll of swansdown calico may be made, and the end of the cylinder used; or a ball of flannel stuffed with cotton-wool; or even a little pellet of cotton-wool may be taken between the fingers and used for small sizes.

A variety of the Blanchard brush, as proposed by Mr. Lyonel Clark, is very useful where large sized pieces of paper are to be coated. A sheet of fairly thick celluloid, such as is used for film photography, is taken; on it is laid a packing of cotton-wool; and, lastly, a strip of swansdown, the swansdown being longer than the celluloid. The three are then doubled back without folding, the overhanging ends of the swansdown folded over the celluloid, and then clipped between two pieces of wood or glass that are sprung together with a broad indiarubber band, and which pieces serve as a handle. The celluloid gives the necessary stiffness without rigidity, whilst the packed swansdown makes a capital spreader.

Fig.2.

Whatever be the nature of the pad used as a spreader, it must not be used more than, say, a quarter of an hour at a time, or preferable even less. The outer coating should go into the residue tub, whilst even the inside packing should be washed in acid and water. This last may be avoided if, in the modified Blanchard brush, a thin sheet of oilskin be placed between the outer swansdown and the cotton-wool packing.

Applying the Solution.

The paper is laid sized side uppermost (and this side may be distinguished by the fact that in the rough paper the rougher, and in the smooth paper the smoother surface, are the sized*), and the measured quantity of the mixed solution is poured on to the centre of the sheet; the pad is then applied, and with a circular motion, with the strokes spreading each time more outward, the entire surface of the paper is lightly gone over taking care to see that every portion of the paper is covered. The direction of the motion is then changed, and up and down strokes are given so as to cross the sweeps at right angles, and so obviate every chance of the coating having a tendency to dry in streaks.

In coating large sheets, it may be advisable to coat portions at a time, pouring a little on at one corner, smoothing that off, then doing another zone, and so on till the whole surface is covered.

It is necessary to coat the whole surface of the paper, even if a vignette be intended, as where the sensitizing solution leaves off, the edges have a tendency to become reduced and subsequently dissolved; but of course the same care need not be expended to see that the coating be as evenly applied at the edges as at the centre.

No difficulty should be experienced in coating a sheet of paper evenly, as the operation is in reality very simple, being far more easy to perform than describe.

N.B. About 20 Minims extra of solution per 26 by 20 sheet should be taken, when coating the first sheet, to allow for the absorption of the fluid by the pad.

Part V.

Drying the Paper.

Some little difficulty, and some loss of paper, may be met with at this point, as it is important that the paper be in a certain condition before it be dried, and therefore the instructions should be carefully followed, and even a few experimental pieces may be profitably wasted.

The drying divides itself into two operations, both of which should take a more or less fixed period of time. The first stage is what may be called the surface drying; this allowed to take place spontaneously, the paper being hung up for the purpose by one end, or preferably, laid down, sensitized side uppermost. It should on no account be hung over a rod. This first drying is simply the evaporation of the surface moisture; this should take not less than five, and not more than ten minutes. If, through excessive climatic dryness, the paper becomes desiccated too soon, artificial means must be resorted to to keep the paper damp a longer period. The second drying operation takes place by artificial means, even in the hottest climates, as it is most important that it be not only quickly but very thoroughly performed.

The sheet of paper then, as soon as the surface moisture has disappeared, is held in front of a fire, or over some gas or paraffin burners, till the remaining moisture is rapidly and completely removed. This drying point is indicated by the change in the colour of the surface, which from a pale lemon changes to a deeper saffron hue, and the paper becomes crackly to the feel. Care, of course, must be taken not to scorch the surface of the paper; but short of this, the drying may be as rapid as possible.

And now a few words as to the reason of this care in drying. It is very evident that the result sought for is to obtain as much of the sensitive salt on the very surface of the paper as possible;

but, at the same time, it must have sufficient hold of the paper not to be washed off in the subsequent operations.

Now, if the paper be dried or allowed to dry too quickly, the solution will not have had time to solder itself, so to speak, to the paper, and in the subsequent operation, will all fall off in the hot developing bath. Whereas, on the other hand, if too great a time be allowed to elapse, the solution will have a tendency to sink right into the paper, and the resulting prints will be flat and foggy. Hence the necessity of adhering pretty closely to the above rules.

CHAPTER V.

PRODUCTION OF PRINTS BY THE HOT-BATH PROCESS.

Preparing the Paper for Printing.

Ordinary printing-frames are, of course, equally available for platinum printing. It is, however, necessary that an indiarubber pad be placed at the back of the paper to guard it against damp during this operation. Ordinary thin sheet indiarubber, such as is sold at all indiarubber stores, is the most suitable for this purpose. It should be the full size of the printing-frame, so as to thoroughly protect all portions of the print. The ordinary rubber-covered fabrics of which mackintoshes are made can be used for this purpose, but they are decidedly inferior to the indiarubber sheeting. This, moreover, makes a nice, soft pad, and, if a plate-glass printing-frame be used somewhat larger than the negative itself, platinum prints can be left with impunity over-night, even in a damp atmosphere. Paraffined paper may also be used at a pinch, but it is not so pleasant to work with as the indiarubber. We cannot too strongly insist on the necessity of keeping the paper dry if prints with rich, juicy blacks and pure high lights are sought for.

Storage of the Paper.

Whether the paper be prepared by ones self, or be bought from the Platinotype Company or their agents, it is absolutely necessary for its preservation that it be stored in damp-tight calcium tubes. These tubes can be obtained directly from the Company, or they can be made by any ordinary tinman. They are nothing else but ordinary soldered tubes, having at one end a perforated compartment containing dry calcium chloride; this is commonly mixed with asbestos, or some fibrous material. The joints of this tube are made air-tight by means of a broad indiarubber band. We find it an advantage to grease that portion of the tube over which the removable end slips; this not only tends to make the joint more air-tight, but it also enables the tube to be much more easily opened and closed.

The calcium chloride itself is best wrapped up in one or two thicknesses of muslin; this prevents any small particles finding their way through the perforated diaphragm and falling on the paper, which it would at once mark. The calcium chloride should be examined from time to time, and when found saturated with moisture it should either be removed and fresh substituted, or else dried. It requires pretty considerable heat to thoroughly dry the calcium. This is best done in a thin iron dish over a Bunsen burner, the heat being continued till the mixture becomes crisp and of a white colour. If asbestos be used as a vehicle, the lumps can be heated till they are red hot, as it will not burn. On first heating the chloride it will appear to become wetter and more flabby; the heating should, however, be continued, till it turns of a white colour, and gets hard and crisp.

Hot-bath platinotype paper should always be stored in such a tube both before and after printing, as otherwise flat and granular prints may result.

Printing.

We will now assume the paper to be in the printing-frame and exposed to the light. We have treated elsewhere of the particular kind of negative that is best suited for reproduction in platinotype; we have now rather to deal with the quality of the light used, sunlight or diffused, bright or dull.

We may first note that the same results do not obtain with platinum paper as with silverthat is to say, hard negatives gain nothing from being printed in sunlight, and feeble ones in subdued light do not gain in value, and the reason of this will be explained hereafter.

As a rule, however, we should say, avoid printing in sunlight. There is a phenomenon, known as solarization, which is very marked and prominent in platinum prints; its ultimate result is to cause a granulation of the parts affected, and a decided loss in intensity of colour, so that the dark shadows become lighter than the surrounding parts.

This solarization has its equivalent phenomenon in silver prints, but in these there is no loss of tone, but the parts assume a metallic lustre, whereas in platinotype the print assumes an orangy, granular appearance, very different from the rest of the print.

The actual result of solarization is not easily discoverable. In silver prints it is undoubtedly a true revival of metallic silver on the face of the print, but it is not quite plain whether the same obtains with platinotype, whether it is metallic iron being revived, or whether it is a phenomenon, like the reversal of the developable silver image, and the ferrous salt is partly reconverted back again into the ferric stage. The phenomenon is not restricted to the hot-bath process, but is equally found in the cold-bath process, showing that the platinum salt does not enter into the phenomenon. At the same time, in the cold bath the ultimate result differs somewhat; instead of the solarized part developing lighter, it has a tendency to become darker, especially when a weak developing solution is used; the deposit then tends to form into masses of flat, dark shadow, granular and devoid of all gradation, giving a somewhat curious impasto appearance to the proof.

As this condition of the provisional image has the power of throwing down the ordinary platinic chloride very freely, it would seem to favour the hypothesis that the iron is reduced completely at these spots. A damp condition of the paper tends to accelerate this proneness to solarization, which is another argument in favour of using pads.

In platinotype printing it is not possible to follow the progress of the printing like one can in silver printing, but a good deal of the image is visibly formed and seen; in colour it is of a purplish tinge, and stands up fairly well against the yellow of the surface.

It is always a difficult matter to describe exactly the point at which the print should be removed from the printing-frame. It is really a matter of education of the eye. When accustomed to platinum printing, one can see a great deal more detail than one could at first; in fact, some of our best workers assert that they can see everything they wish to bring out. Undoubtedly, if at the edges of the negative the paper be protected by an opaque mask, so that one may have a portion of the paper that one knows has not been subjected to exposure to refer to, it is really possible to see a great deal of the detail. As a rule, one should print till the detail in the half-tones just shows; for instance, taking a portrait, all the detail in the shadow side should show, and the outlines in the lighted side, but the details in the hair and face on this side should not do so.

As a rule, beginners will be found to considerable over- expose their prints; on development these come out flat, and hence the general theory that it requires very hard negatives to get good prints. The real cause of this, we think, is not an affair of getting out more or less detail, but rather an affair of intensity. Workers accustomed to the gradual and visible darkening of silver paper cannot believe that the faint lilac image on the platinum paper can ever give them the deep shadows silver printing has taught them to expect.

We must, in platinum printing, banish all thought of getting density on the print whilst in the frame, and simply look to the appearance of the detail; if this be done, we opine that the worker will have no difficulty in rapidly obtaining a complete mastery over platinum printing. At the same time, it must be remembered that different preparations of the paper may give results more or less visible before development, and we think old platinotype workers will bear us out when we say that the present brands of paper as fold by the Company give a much more visible image than that sold by them some years back.

Whilst the constant worker in platinotype will, we feel sure, find no difficulty in always correctly exposing his prints, yet the amateur, with his intermittent printing, may not be so successful. To such workers we cannot too highly recommend the use of a sensitometer. It is really totally immaterial what sort of sensitometer is used; any paper or plate that is divided into squares or parts having different opacities or power of resisting light, will do. An excellent one can be made on silver or platinotype paper itself.

Take a slip of sensitized paper, and divide it by pencil lines into, say, twenty divisions; now expose these divisions to light in the following ratio: the first one 1 second, the second 1 ½, the third 2, and so on, so that each third division has twice the exposure the first had, thus:1, 1 ½, 2, 3, 4, 6, 8, 12, 16, 24, 32, 48, 64, 96, 128, are the ratios of the exposure. What the actual times of exposure should be, depends, or course, on the light; the longest exposed parts of the slip should be so arranged as to get maximum blackness. Each division of this slip is, after development, then marked with any consecutive figure or letter. Whilst the negative to be printed from is being exposed, a slip of paper, cut off from the edge of one of the prepared sheets of platinum paper, is placed underneath this graduated slip; the print is examined from time to time, and when it is considered to be finished, removed from the printing-frame, at the same time the trial slip is removed from under the graduated sensitometer, and the last number visible, without developing, is recorded.

If, after the print has been developed, it is found to be correctly exposed, the number read off under the sensitometer is the key number of the print, and wherever or in whatever light the negative be again printed from, it is not necessary to examine the print at all, but when the key number just shows on the strip under the sensitometer, the print is finished.

Should the first print not be correct the first time, one has only to expose fresh prints and fresh slips till higher or lower numbers on the sensitometer are brought out, in accordance whether the print was found to be over or under exposed. By this system of trial and error, the key number of each negative will rapidly be fixed on, and, once found, should be written on the negative. We feel sure that all workers who will take the little extra trouble there is required to work thus with a sensitometer, will be speedily rewarded by the saving they will effect.

Rapidity.

A good deal has been said and written about the rapidity of platinum prints. It is generally stated that they are three times as rapid as ordinary albumenized silver paper. It is, of course, a matter of extreme difficulty to make any experiments in the relative rapidities of the two classes of prints, as ordinary silver paper varies so much in rapidity, according not only to variations in its preparation, but also according to its age, manner of keeping, etc.

On the whole, we doubt whether platinum paper has any very great advantage over silver paper in good condition, and if the latter be home sensitized and fumed with ammonia, it certainly has none; at least, it will have but slight advantage if the light be good, but when we come to the yellower light of winter, platinotype has certainly a great advantage over silver. The explanation of this is to be sought for in the different behaviour of the salts of iron and silver under the action of the spectrum.

Development.

After removal from the printing-frame, the proof is to be stored in the calcium tube till such time as it may be convenient to develop it. This development is normally effected by wetting the surface of the print with a hot solution (160 degrees to 180 degrees F.) of neutral oxalate of potash.

This solution of oxalate is not quite a saturated one, the quantities usually given being 130 grains to the ounce; but it rapidly becomes so through evaporation, after being heated once or twice. It is, therefore, our practice to commence with a saturated solution, having always the crystals in excess. One reason for this is that there is no danger of the oxalate solution becoming spent, as the fresh crystals always keep it up to the working point.

As the development of the print is practically instantaneous- -that is to say, the greater portion of the platinum is substituted for the iron on the first contact of the oxalate the method usually adopted is to float the sensitized surface of the print over the surface of the oxalate solution. For this purpose the oxalate is contained in an iron dish considerably larger than the print to be developed; the particular kind of dish mostly used is one that is employed in cookery, the inside of which is covered with a white enamel that is stated to contain no lead in its composition.

This dish is placed on a gas or other heating apparatus, and warmed till it attains a temperature of 180 degrees F.; this is known by keeping in the liquid a small thermometer (graduated up to 212 degrees F.) closed in a glass tube. This is not a very accurate method of guaging the temperature of the bath, as if the thermometer be moved and placed directly over the flame, it will indicate a higher reading than if left at the side of the dish. However, the exact temperature is of no great importance, there being no practical difference observable between temperatures of 160 degrees and 180 degrees F.

The print is then seized by the two opposite corners, one in each hand, and the nearest edge to the operator, the one held in the left hand, lowered on to the surface of the liquid; the right hand is then moved away, and lowered at the same time. In this way the print can be placed on to the liquid with on continuous sweep. Any stoppage in the lowering will infallibly cause a line along the line of stoppage. It is surprising how adept one gets at floating the paper after a few trials, and not a single piece of paper need be spoilt in this manipulation.

A further advantage of putting the paper down in this way is that it drives any bubbles or scum that may be on the surface of the developer away before it. At times, however, bubbles will be formed. It is advisable, therefore, directly the paper has been lowered on to the developer, to pick it up again by one end and see whether any bubbles have been formed. If so, the bubble should be broken, and the print again be lowered on to the liquid, when the place protected by it will be developed, and if the bubble be small, no trace of its presence will be left. But if the bubble be large, we have invariably found that a distinct insensible line is left, following the outlines of the bubble.

Time of Development.

The development of the hot-bath platinotype is almost instantaneous, and the image is formed almost directly the print is placed on the bath; at the same time, by leaving it on the bath no ill effects are to be apprehended. In practice, the print is left on about ten to fifteen seconds.

Fixing and Washing.

After removal from the developing dish, the prints are immersed in a bath of hydrochloric acid and water (1 in 60), and left in here ten minutes; they should then be transferred to a second dish of the same strength, and allowed to remain in it about five minutes. After this, they should be again passed through a third bath of the same strength. If this third bath shows any signs of yellowing, the prints should be treated to a fourth. In all cases, the last bath should show no signs of yellow discoloration after the prints are immersed in it.

In practical working, all these baths are not made up fresh every day, but used in progressing orderthat is to say, the first bath of yesterday is thrown away, and the second bath of yesterday becomes the first of to-day, and so on.

Economy, however, is not to be sought for at this stage, for the only weak and attackable point in a platinum print is its liability to discolour in the high lights if iron be left in the paper.

After removal from the last acid bath, the prints require about ten minutes good washing, when they are ready for drying, trimming, and mounting.

Variations in the Temperature of the Developer.

The temperature of the developer has a somewhat distinct influence on the density curve or scale of gradations of the print. We mean by this that, supposing the slip of graduated paper which we have used as a sensitometer to be divided into twenty parts, and by the ordinary development, when No. 1 square showed the least darkening, No. 10 would then show the most darkening, all the higher squares having the same intensity. If we, however, alter the temperature of our developer, we should find that, although the square that showed the least darkening had not altered, yet the No. 10 square, that gave the maximum darkness, would no longer do so, but the darkest point would be obtained at a higher number.

Let us examine the practical effect of this. The sensitometer is in reality nothing but a simplified negative that contains, however, every gradation from half-tone up to deepest shadow. If we take the first ten squares, we shall be representing a thin negative, all half-tones and no heavy deposits; but if we include, say fifteen squares, we shall represent a brilliant or hard negative with every gradation in it. Now, we see that by varying the temperature of our developer we get identical results from both portions of the sensitometer. A hot developer will bring the tenth square up to maximum blackness, whereas with a cold developer it will only be the fifteenth square that attains this desideratum; therefore, when printing from a thinnish negative, the developer should be used as hot as possible, whereas, when the negative is hard, the developer should be used cold, or nearly so. The converse of this is, that if brilliant results are wished for from an ordinary negative, the developer should be used very hot, whereas, if soft results are to be obtained from the same negative, the development should be with a solution at about 80 degrees F.

We would refer those interested in this question to the special chapter on the subject in the Appendix.

We will recapitulate here the best procedure to follow for different kinds of negatives, assuming that a normal effect is to be obtained.

Thin Negative.Print in the shade or under ground glass and give as short an exposure as practicable, and use as hot a development as possible.

Normal Negative.Given full exposure, and develop at about 160 degrees F.

Hard, Dense Negative.*Give bright light or sunshine very full exposure (sunlight is useful); develop on a bath at 60 degrees to 80 degrees F. N.B.In this cold development, take care that the bath is not in an acid condition, or granularity may result. The bath may also be advantageously diluted with water.

We leave it to the intelligence of the reader to fill up the gaps between these cardinal divisions.

Class of Negative Suitable for Platinotype.

A good deal has been written anent the peculiar quality of negative that is required for platinum printing. It is generally stated that what is known as a hard negative is an absolute necessity. Now, it is of course very difficult to precisely describe what is exactly meant by a hard or soft negative, and different workers may have very different ideas on the subject. From a series of trials that we carried out some time ago, we find the density curve of platinum paper developed at 160 degrees F., and commercial sensitized albumenized paper, to be about the same. This proves what practice has shown us, that the negative that gives a good, plucky silver print will also give a good, plucky platinum one. At the same time, it is more easy to obtain a passable print from a thin negative on silver paper than it is on platinum. But if the instructions for the treatment of a weak negative that we have given above be followed, the difference will not be very noticeable.

In our above remarks we refer, of course, only to platinum paper as sold by the Company. We have shown in the instructions for preparing the paper how the platinotype may be rendered capable of giving hard results from thin negatives. The same obtains with silver paperwhich is assumed to be any good commercial brand; with a homemade silver paper that has been heavily salted, and excited on an ammonio-nitrate of silver bath, good results can be obtained from extremely thin negatives.

After-Treatment of Paper.

Whilst still in the washing water, , platinotype prints have a beautiful glossy appearance, but after drying they naturally lose this gloss, and dry matt. Although this is considered a great advantage by many, yet there are some who still prefer the polished surface. Platinum prints can be burnished in the ordinary waythat is, a solution of Castille soap in alcohol is rubbed over the mounted print, which is then passed through any ordinary burnisher.

Another method, due to Leon Vidal, which will be found fully described in the Photographic News, 1886, p.829, is as follows:Half an ounce of borax and one dram of carbonate of soda are dissolved in ten fluid ounces of boiling water; then two ounces of powdered white shellac are added, and the boiling continued till the shellac is dissolved. Any loss by evaporation is made up, and the liquid filtered through charcoal. The print is floated on the warm solution and hung up to dry, when it will be found to have a slight gloss.

Retouching or Spotting Platinotype Prints.

The platinum deposit being directly on the surface of the paper, it is of course an exceedingly easy matter to stop-out any imperfections of the print by means of ordinary water- colours. This absence of all surface glaze also renders the prints particularly available for colouring purposes, as washes can be laid over these prints with as great facility as on ordinary drawing-paper. The only danger is that the print, through a too long sojourn in the acid clearing baths, may have lost all its sizing and become porous, in which state it would be necessary to re-size it in the ordinary way. The colour of the deposit varies from brownish-black to black and bluish-black, and therefore the colours most useful will be a mixture of sepia, indigo, and india ink.

We need hardly point out to artists the value that the platinotype has for all purposes where a photographic basis is to be used. All kinds of paper or stuffs can be easily prepared according to the formula given in another part of this work, and by the use of suitable negatives, a thin, delicate impression, containing every detail, but having no intensity, can be obtained, over which the picture may be finished either in pastels or water-colours, or, if suitably sized, even oil-colours.

Failures: Their Causes and Remedies.

1. In self-prepared paper, general fog; otherwise, the pictures are good.

a. The paper was affected by light during the sensitizing or drying. The remedy is obvious. A slight reduction in the platinum print not being observable till after development, particular care should be taken during the preparation of the paper, and no reliance be placed, as in ordinary silver printing, on the appearance of the paper under treatment.

b. Too high a temperature in drying; this should not exceed 104 degrees F.

c. The ferric solution has gone bad. The ferric-oxalate solution, being destroyable by light, should be carefully stored in the dark. To test any doubtful solution, add the ferri or red cyanide of potassium, when, if any ferrous salt be present, it will strike a blue precipitate. If the ferrous salts are only slightly present, the red prussiate will restore it again.

2. The prints are weak after development.

a. Paper has become damp. In this case granularity is generally a concomitant of weakness. We have already spoken fully of the remedy. If such paper is not seriously affected, something may be done by over- printing, and developing on a cold, diluted bath.

b. The paper is too old. In this case the results are characterized both by fog and weakness.

Mr. Burton gives (British Journal of Photography, xxxviii. p. 421) a method by means of which old or spoilt platinotype paper may be made serviceable by adding potassium hypochlorite or sodium hypobromite to the developing solution. He gives no formula. We have found that chloride of sodium (table salt), added freely, and ounce or so to the pint, kept the whites clear in commercial platinum paper that had been left in the damp for over a year. The proof was, of course, considerably over-printed. Willis recommends potassium chloride as a restrainer. Burton also notes that, with fresh paper, the hypobromites and chlorites tend to give hard results.

3. The prints are vigorous, but come out flat after drying.

a. Cause: lack of sizing of the paper, whereby images sink into the substance of the paper. Remedy: with such paper employ more of the gelatine or arrowroot sizing.

b. The drying of the paper has been too slow. Remedy: we have already treated of the precautions to be observed in drying; ten minutes is about the correct time.

4. The prints on development are vigorous, but the platinum black falls off in the developer.

a. Too rapid drying, causing the iron and platinum salt to be formed on the very surface of the paper itself, and have no cohesion; or it may arise from using a paper with a hard glaze, and not having sufficient sizing in the sensitizing solution to enable this to lay hold of the glaze. Remedy: see the last failure.

5. The paper is yellow in the high lights. This may arise from several causes.

a. The sensitizing solution is not acid, and an insoluble basic precipitate of iron has been formed in the paper. Remedy: follow the instructions more carefully.

b. Paper that has been blued with ultramarine will turn a yellow colour after treatment with iron. Remedy: when using an unknown paper, trials should be made to see whether the paper suffers when in contact with hot oxalate of potash or hydrochloric acid.

6. The prints after development are too hard.

a. Too short an exposure.

b. Too much chlorate in the sensitizing solutions. The remedies are obvious.

7. Spots and streaks: dirty brushes, pads, or fingers. Wavy streaks are frequently caused by the surface portions of the sensitizing solution being reduced by keeping, or having been already used and returned to the stock. Remedy: cleanliness, and use of fresh solution each time.

8. Black spots.

a. Minute particles of metal, chiefly brass or iron, in the texture of the paper itself; these set nuclei, around which there is a violent deposit.

b. The iron is sometimes carried up by the Bunsen burners used in drying the paper.

c. Or such spots may also be due to impurities, or even metallic platinum in carelessly prepared chloro- platinite.

Remedies.Use a purer sample of paper, and examine sheets carefully by transmitted light for minute specks.

b. Use brass Bunsens, or, better, brush or clean them out well.

c. Filter the solution.

If the ready-sensitized paper is bought from the Company, it is assumed that no fault will be found in it, and therefore all failures are attributable to the subsequent manipulations. We have first the obvious

faults and their more obvious remedies of over and under exposure, the one shown by general fog and flatness, the other by great hardness and want of detail.

Granularity may be caused on the best sample of paper by damp; keep it, therefore, scrupulously dry.

The developer can be used over and over again, but at last it will become weakened and saturated with iron salts. Indeed, the bottom of the bottle may be full of crystals of potassio-ferric oxalate, and still the developer work well. Sometimes, however, prints come off the bath weak from a spent developer. The developer should therefore always have undissolved crystals of oxalate of potash at the bottom, and the water evaporated off at each heating can then be made up again. Such a developer will keep a very long time; when it gets, however, very yellow, it is best to make up a fresh one, throwing the old one away.

Black spots on the prints are sometimes caused by particles of iron that fall on the print if it is cut by a steel knife, or more often they are particles torn off the calcium tube in opening or shutting it. Fold and cut the paper, therefore, with a bone or ivory knife, and wrap it up in paper when in the tube.

Spots and streaks, black or white, may be caused by any dirt or impurity allowed to fall on the paper. The finger will nearly always leave an insensitive mark; the paper therefore should be handled as seldom as possible, and never touched on the sensitized side.

The faults that arise from careless development will generally take the form of bubbles of a lighter colour than the surrounding print, or else form lines with a lighter edge across the print. The bubbles have already been referred to, and the cause of the lines is a stoppage in lowering the print on to the surface of hot oxalate solution. A little practice is required to put the paper properly, without stopping, in one sweep on the surface of the hot oxalate.

CHAPTER VI.

Variations in the Hot-Bath Process.

Production of Sepia Tones.

The natural tone of the paper that we have hitherto described is of either a blue-black, or at best a dull black without any warmth or richness. By certain additions, however, to the sensitizing bath, the image may be produced in a fair variety of warm tones, from a warm engraving black down to quite a hot sepia. The Platinotype Company sell a special paper which they call their sepia paper, and to the special manipulation of this we shall allude in due place. We will now proceed to the examination of the formula proposed for the production of these warm-toned papers.

The cause of the warmth is undoubtedly due to the presence of mercury in the sensitizing solution, but whether the actual colour of the print is due to an amalgam of the mercury and platinum, or whether it tends to keep part of the platinum in the form of an oxide, or whether the mercury may permit of the platinum forming an organic salt with the colloid on the paper, is not clear. It is, however, certain that the colour of these sepia prints is not so stable as that of the black ones, and in the fixing bath they will change colour slightly, losing somewhat their sepia tint. The change is very slight, and would be absolutely unnoticeable in any other process, but a platinotype print is usually such an unchangeable thing under every condition, that even this slight alteration is remarked.

The following formula for the production of these sepia prints is given by Lainer (Photographische Correspondenz, vol. xxx. p. 325):

Chloro-platinite of potassium solution,	1 in 66parts.
Normal iron solution	2.5parts
Normal chlorate solution	3 parts
Bichloride of mercury, sat. sol.	1.2”

The iron and chlorate solutions are the same as those used for the ordinary hot-bath process (see p. 58, ante).

T.T. Sachers (see Photographic Timer, vol. xxi. p. 489) records some experiments made in the direction of obtaining sepia paper of a warm tone. He finds that using the formula of Pizzighelli, a 10 per cent. addition of a 1 in 20 mercuric chloride solution to the sensitizing bath, gave a rich brown print, having the half-tones of a homogeneous colour, and the whites clear. If in addition to this amount of mercury added to the sensitizing solution, a further amount of about 2 per cent. of the salt be added to the developer, the prints will be of a warmer or hotter colour, abut the half-tones may have a yellowish tinge.

From the results of his experiments it may be assumed that an addition of about ½ grain of the mercuric chloride salt per 2 drams of the sensitizing solution is a safe amount, although this may be increased for special cases.

The general manipulation of the preparations of such paper is of course identically the same as in the ordinary hot-bath process, and the only fault proper to this process, likely to be met with, will be getting a too great quantity of the mercury in the sensitizer. This is characterized by first the half-tones of the prints assuming a more yellowy brown than the deep shadows, followed, if the mercury is in excess, by an absolute degradation of the high lights themselves.

Manipulations of the Sepia Paper of the Platino- type Company.

During printing the treatment of this paper differs in no way from the ordinary paper, and the same care must be exercised, and the printing carried on to the same depth. The development can be, and indeed is, carried out by many good workers on precisely the same lines as the ordinary black paper, that is, using the same baths. The Platinotype Company, however, sell a special solution for mixing with the ordinary developing bath. The object of this is to preserve the whites from degradation. Some workers add a small amount of mercuric chloride to the developing bath as well, but the results appear to be uncertain. It may be noted that the bath used for sepia prints, and especially one that has had mercury added to it, should not be used again. Several prints may be developed on it in rapid succession, but it must not be put aside for another day, and even in current use the least sign of degradation in the whites of the prints should cause the rejection of the bath. The after- manipulations are exactly the same as with the ordinary paper.

The sepia paper of the Company is an extremely variable paper in its colour, but of late it has been much improved in that respect, and the later brands of the paper show a much truer colour, being, indeed, homogeneous throughout, and not, as the old paper did, showing a sometimes decided difference in tone between the shadows and the high lights. In the Appendix, where we dwell upon what we may ter the higher development of platinotype prints, we have given some special developers for this brand of paper for cases where special effects are required.

After-Modifications of Black-Toned Platinotype Paper in Order to get Warmer Colours.

We have already mentioned that by the addition of mercuric chloride to the developing solution, the colour of the sepia prints can be altered, and this also holds good in the case of the ordinary or black paper. A small addition, say about half a grain to the ounce of dry mercuric chloride, will generally warm the tone of the print, but more than this is a risky proceeding, as frequently the double toning, alluded to before, takes place, whilst the whites of the prints will also be frequently degraded.

Another method of altering the colour of platinotypes, and one that has been experimented upon by many workers, is by means of toning them with other substances, or more properly to speak by intensifying them, as the change of colour is effected by precipitating on the image some other coloured substance. Vogel appears to have been the first worker in this direction, although it is true he worked only with the idea of intensifying and not altering the colour. He describes (Phot. Mittheilungen, 1887, p. 233) how he mixed a solution of chloro-platinite of potassium with an ordinary dry-plate developer, and flowed the same over a feebly printed platinotype. In a short time the solution turned black, and metallic platinum was thrown down, and attached itself preferably to the existing image on the print. The process is interesting, but cannot be regarded as a success, although at the same time it is highly probable that, in the presence of a reducing agent more under control than the one he used, it could be made into a practical process.

The first worker, however, who produced a practical process for toning or intensifying platinotypes was Roland Briant (Camera Club Journal, vol. vi. p. 115). Briant worked on the lines laid down by Lyonel Clark in his process for altering the colour of silver prints toned with platinum or other metals by the precipitation thereon of metallic silver, from a solution of the nitrate in conjunction with acidified gallic acid. Briant gives the following formula: About 5 to 10 drops of glacial acetic acid, 1 grain pyro, and about 2 drops of a 60-grain-to-the-ounce solution of nitrate of silver is made up with water to 1 ounce, and poured over the print. The actual proportion of the ingredients varies with the temperature, the idea being just to get the silver on the verge of being thrown down or reduced. Increase of pyro or silver naturally increases this tendency, whilst increase of the acid retards it. If the solution is gradually brought up to the right point, the silver will begin to first deposit itself on the image already formed, leaving the high lights quite clear, whilst the solution itself also remains colourless. The colour of the deposited silver is a rich red brown, and the tones given thereby are very pleasing. The action is an intensifying one, and tends to harden the print, so that flat proofs give the best results. Briant experimented with the ordinary hot bath, with prints developed with the addition of mercury, and with the ordinary sepia paper. He also notes that if required the silver image can be again toned with gold, uranium, or any other agent, and the colour again be modified, or the print may be treated with mercury and again intensified.

Mr. Fitz-Payne (Camera Club Journal, vol. vi. p. 161) carried on independently Briants experiments with uranium, and notes that platinotypes, if they have been carefully fixed so as to dissolve out all the iron salts, can be toned with the ordinary uranium intensifier to any tone from a rich brown to a Bartolozzi red. His formula is as follows:

A. Glacial acetic acid	1 dram.
Uranium nitrate	0 grains.
Water up to	5 ounces.

B. Ferricyanide of potassium	10 grains.
Glacial acetic acid	1 dram.
Water up to	5 ounces.

Just before using, mix equal parts of A and B, and flow over print. The change in colour will take place slowly, and when the desired tint is obtained the print is rinsed, rather than washed, as the uranium salt dissolves out in water, and therefore if intensification has been carried too far the print can be reduced by simple washing.

Strakosch (Photographische Correspondenz, vol. xx. p. 169) gives the following method of obtaining prints of a warm colour. In the first place he adds from 1 to 2 parts of a 4 per cent. solution of mercuric chloride to the developing bath. This produces prints having already a brownish tone, which are then placed in the following bath:

Nitrate of uranium	10 grams.
Ferricyanide of potassium	2 grams
Glacial acetic acid	60 grams
Water up to	1 litre.

In this bath the prints turn of a rich sepia colour, getting redder as the toning is continued. When the desired colour is obtained, the prints are lightly washed in water slightly acidulated with acetic acid, and then rinsed in pure water. Strakosch also notes that these prints if treated with ferric-chloride assume a green colour.

It is urged against prints toned or intensified by uranium that they are non-permanent, but what is probably a more serious objection is the fact that the uranium is practically deposited to an equal depth all over the image, and so whilst it modifies the half-tones very considerably, the dark shadows, where the quantity of platinum present is very large, are not modified to anything like the same extent, and we get double toning. If is probably for this reason the Strakosch first browns his platinotypes with mercury, as then the mixture of the red uranium with the brown image would be more homogencous.

Another method by which the colour of platinotypes can be modified is that described by A.W. Dolland (Photograph Journal, 1894, p. 189), and consists in a precipitation on the image of metallic gold. From the result of several experiments Dolland gives the following bath as acting well;-

Gold terchloride	15 grains.
Water	7 ½ drams.

The print is first wetted, and covered, by means of a brush or pledget of cotton-wool, with glycerine. When evenly covered a little of the gold solution is poured on and kept moving so as to touch equally all parts of the print. The print will soon begin to increase in strength, assuming a blue-black colour, and the action may be allowed to continue as long as the whites remain clear. When finished the glycerine and gold is washed off the print, and the same sponged over with a weak developer, the following being a good one:

A. Sodium sulphite	1 ounce.
Metol	.50 grains.
Water up to	10 ounces.

B. Potassium carbonate	1 ounce.
Water up to	10 ounces.

For use, mix equal parts of A and B. The use of this developer is to completely reduce to the metallic state any gold that may be left in the pores of the paper, which otherwise would turn pink on exposure to light.

Dolland notices that although old prints, that is those kept three or four weeks, can be treated in this way, still new prints work more easily.

It should also be noted that the above process is a real intensification, and quite faint prints are brought up by it to full density; indeed it has been noticed that detain which was apparently invisible in the print was brought to view by it. In this respect this process differs from the uranium one, which acts more as a stain, and modifies the colour considerably without intensifying the print to any great extent.

The chemical action of Dollands process is interesting, and has given rise to some discussion. Gold in the presence of glycerine is certainly thrown down, as Dolland showed; but the action is very slow, and only takes place rapidly in the presence of the platinum image. This fact has been put down to the platinum, whose power of absorbing hydrogen is, of course, well known; but it is doubtful whether the real cause is other than physical, being, in fact, the same that causes the silver in the experiments of Clark and Briant to only precipitate itself on the already formed image. In connection with this point Liesegang, whilst repeating the experiments of Clark and Briant (Photographic Work, 1894, vol. iii. p. 21), noticed that many other colouring matters would in the same way preferable attack the already formed image, whilst leaving the paper white. Amongst others he notes that alkaline pyro, or amidol and carbonate of soda, tend to stain a platinotype of a brown colour, leaving, however, the whites clear. He also noticed the same action with carbon and Woodbury prints, showing that in this case, at any rate, the platinum has nothing to do with the matter. It would be interesting to repeat Dollands experiments with carbon and silver prints, and see whether gold would be deposited thereon in the same way as on the platinum ones.

Extra Rough Platinotype Paper.

Amongst the papers lately introduced by the Platinotype Company is one having an extra rough surface, similar in quality to the rough surface drawing-paper used by artists. Without being altogether a sepia paper, the colour of the prints produced on it is of a rich, warm tone, varying somewhat, it is true, with different batches, but generally tending to greater warmth as the paper becomes old. It appears to have especially good keeping qualities, and we have experimented with some that had kept for over a year in an open case. Although not in the best of conditions, we found that by adding a good amount of common salt to the developer, and using the same cold, we got very good prints of a warm colour, with the high lights only slightly degraded.

In general use, the treatment of this paper is exactly the same as that of the ordinary paper, but it is almost a necessity to print with an actinometer, as, owing to the grain, it is extremely difficult to detect the extent to which the paper is printed, and the image apparently shows but feebly in the frame. Under any conditions it requires a longer exposure than the ordinary paper. Its after-treat- ment, also, is the same as that of any other paper, and it is amenable to the same variations in development; but it may be noted that it is not successfully amenable to after-treat- ment with a view to altering the colour. Paper of this quality is much used by some of our best workers, as the grain tends to destroy too prominent detain, and at the same time lightens up any large masses of dark shadow.

This paper should be handled with care, even in the tube, as if two pieces are allowed to rub together, the pressure acting on the tops of the grain will frequently cause the platinum salt to be reduced, and in the bath these points will come up as darkish specks. They are too small to be noticeable except under close examination, but they tend somewhat to generally reduce the purity of the high lights. The same applies to the treatment of the wet print, as the surface is very tender and easily abraded, although it is probable that when the latest improvements in the manufacture of the platinotype paper are brought to bear on this brand, this fault will disappear.

Stuffs.

The Company have also of late prepared a large variety of linen, silk, and other stuffs, which have been used by some workers with success as a basis for ordinary pictures. The effect produced is that of a picture on canvas, but the prints suffer from the fact that they look as if they were copies of painting, rather than original studies. At the same time, in certain conditions and for certain purposes, the regular grain of the materialsilk, calico, or satin jean, or whatever it may behas a certain value. There is nothing that calls for special comment in the treatment of the stuffs. Of course great care must be exercised in the printing to see that the stuff lies flat and does not move in the frame when examining it, and therefore it is preferable to always work with an actinometer. We ourselves, in working on thin silk, have found it useful to mount the stuff on a light stretcher, like an artists canvas is mounted, cutting down the back of the printing-frame for this purpose. The silk is left on the frame till all the manipulations are completely finished, and allowed to dry thereon. Development is carried on in the same way, but the print should, of course, be immersed bodily in the developer, and not floated on it.

CHAPTER VII.

Platinum in the Bath Process.

This process, introduced by Willis in 1888, was originally known as the cold-bath process, but in order to avoid confusion with the 1892 process, now also generally termed the cold-bath process, we have given it the original designation as proposed by Willis himself.

Although not a commercial process at the present time, it having been supplanted by the later 1892 process, which produces most of the effects obtainable by it, still it is one of very great beauty and simplicity, and it has the advantage that the inventor has in this case himself given the formula for its preparation. From the aesthetic point, this process is remarkable for the rich velvety brown blacks obtainable by it, quite different in their colour from the sepia browns of the older process, whilst the fact that the platinum salt, instead of being added to the sensitizer, is mixed with the developer and brushed, so to speak, on the surface of the paper during development, gives a very remarkable brilliancy of image. No better distinction between the appearance of the results obtained by the old ho- bath and this new process can be given than by stating that, whereas the former recalled, in its blue-black brilliancy, the idea of a steel engraving, the latter, with its rich warm tones, was comparable to the best mezzo- or aqua-tint work.

These warm tones are to some extent obtainable by the present processes, but we were so fascinated with the first one that it is with regret that we notice its withdrawal. As we cannot help thinking that it may again come into use, and as its preparation entails no difficulty, we propose to devote a short chapter to it.

The rationale of this process is the formation of a preliminary image in an iron salt, the reduction of this by exposure to light, and then the application of a developing substance containing the platinum salt, which is then thrown down by the reduced iron of the image. This process is undoubtedly the natural form that a platinum printing process should take, and it is, therefore, not surprising that, as Willis states, this was one of his first experiments. The difficulty met with, however, was the fact that the provisional iron image was dissolved out by the developer before it had time to reduce the platinum salt. Willis, however, subsequently overcame this fault by adding a substance to the provisional image that accelerated the reducing power of the iron, whilst at the same time he added another ingredient to the developer that retarded its tendency to dissolve out the provisional image. These salts were the addition of mercuric chloride to the sensitizer, and of a phosphate to the developer.

The preparation of paper for this process differs from that for the ordinary process only in the fact that the platinum salt is omitted, and from 1 to 1 ¼ grains of mercuric chloride are added to each ounce of the ferric-oxalate sensitizing solution. The paper is coated with this solution in the ordinary manner, and a sheet of paper should then have about 13 grains of ferric oxalate, and 1/10 grain of mercuric chloride, to each square foot of surface. The paper is dried and stored in the usual way. The appearance of the surface of the paper is of a much lighter tint than the old process, owing to the absence of the platinum, being, in fact, of a lemon-yellow colour, whilst, during printing, the appearance of the image is less visible than in the hot-bath process; but this may vary with the kind of paper and also with its hygrometric condition, the damper that paper the less visible being the image. This brand of paper will also be found to print slightly more rapidly than the old kind.

A remarkable feature in this process is the fact that the precautions for always keeping the paper dry, so necessary in the old hot-bath papers, are here unnecessary, and indeed, for certain effects, the paper has actually to be damped before developing. It is, however, not advisable to let the paper get damp before printing, although this will not be injurious in all cases; but it is best to store it in the ordinary way, and then, after printing, either damp the paper by leaving it in a drawer overnight before development, or, what is perhaps simpler, by actually steaming it over hot water. Willis recommends that the proofs when removed from the frames should be stored in flat cardboard deed-boxes. If stored in a tin it is advisable to roll the prints sensitized side outwards; this makes the prints more amenable for floating on a small amount of developer, and as this contains platinum, it is evidently an advantage to use as little as possible, and prints curving outwards are of course more easily floated than those curving inwards.

The normal developing solution is made up as follows: A mixture of neutral potassic oxalate and mono-potassic orthophosphate (termed bythe Company the D salts, and sold ready mixed by them), in the proportion of two of the former to one of the latter. Half a pound of these mixed salts is dissolved in 50 ounces of warm water. The chloroplatinite of potassium is dissolved in the proportion of 60 grains in 2 ounces of water (this is called the P solution). (Ordinary water may be used for the D solution, as any precipitate will settle when cool, but it is advisable to use distilled water for the platinum.) In normal work the D solution is diluted by the addition of two parts of water to three of D, which gives a strength of about 1 in 10 ½. The actual developer is made up by taking 5 parts of the diluted D solution and adding to it 1 part of the P solution. This will be about equivalent in round figures to

Potassium oxalate	53 grams	or 23 grains.
Mono-potassic orthophosphate	27 grams	or 11 grains
Chloro-platinite of potassium	11 grains	or 5 grains
Water	1 litre	or 1 fl. ounce.

It will take about 1 to 2 ounces of the above to cover the bottom of an ordinary whole-plate dish, but this quantity can be reduced by using dishes with plate-glass bottoms. Mr. Clark showed a dish of this sort supported on three leveling screws, and having sides of only ¼ inch deep, by means of which he reduced the quantity of developer to about 1 ounce for a 12” X 10” print. The print is floated on the developer in the usual way, and as the paper may be fairly damp at the time of floating, it is an easy matter deal with a thin layer of liquid without making bubbles and marks. Directly the whole of the print is placed on the liquid it may be at once lifted up and the image examined. Its first appearance is of a greyish colour, and any masses of shadow may show signs of granularity. At this time any bubbles may be broken, and, if small, will probably not show. After a few seconds, during which the print is held in the hand and watched, it is again placed on the bath, to imbibe more of the solution, when it will rapidly darken, tending to a warm black, and all the granularity in the shadows will disappear. If there is still a want of vigour in the shadows, the print may again be placed on the bath, by which means the utmost vigour will be obtained. The resulting print will be of a rich brown-black colour, especially if it should have been damped before developing. In the case of small prints, that is up to whole plate, they may be developed by means of a brush in which there is no metal fastening that can come in contact with the developer. The brush must be well filled with liquid, and the strokes given with it must be decided and rapid and overlap each other, or streaks will show. In the case of landscapes it is advisable to commence with the sky portion.

The brush method is an economical one as regards amount of developer, but a little practice is required so as to prevent the overlapping of the strokes showing. Above whole plate size we cannot recommend the use of the brush, unless, of course, tools of a very broad type be used.

As a general rule it is preferable to use fresh developer for each piece of paper, as naturally it takes up after use a good amount of the iron salts from the paper, which will eventually cause a complete reduction of all the platinum. Old developer may, however, be kept for a short time, and for certain effects it, with the addition of a little fresh platinum, often makes a good developer twice, is that a scum generally forms on its surface, which comes off on the next piece of paper floated, and marks it with wavy discolorations. This can be remedied by skimming the developer after each print has been floated, and in cases where several prints are consecutively developed on the same bath it is a necessary precaution.

The further manipulations of this process do not in any way differ from those in use in the ordinary hot-bath process, and call for no further remarks.

This process is remarkable from the fact that it gives the operator great facilities for producing different effects by varying the components of the developer. As regards the proportion of the two salts that make up the D solution, there is but little to be gained in altering them; but considerable variations can effected by altering the strength of the D solution, and also its proportion to the P salt.

By decreasing the quantity of D, the developing action is accelerated, the tones given are colder, and there is a greater tendency to granulation, whereas by increasing the quantity of D the reverse is the case, whilst at the same time there is also a tendency to destroy half-tones, that is, to give a shorter scale.

On the other hand, an increase of P gives increased vigour and perhaps richer tones, whilst its decrease gives the opposite effect. At the same time, the duration of development affects also this variation, and a print if floated longer on a solution weak in P will, within limits, give as strong an image as if P had been normal.

Variations in the tone or colour of the resulting prints can be obtained by suitable means. The preparation of the paper has, as in all the other processes, most to do with this, but the colour is also largely affected by the degree of dampness of the paper at the time of development. If the paper, after printing, be actually steamed until it is quite flabby to the feel, and developed in this state, very warm tomes are obtainable, and it would look as if some organic salt were formed between the iron of the image and the colloid of the paper, that altered the general character of the platinum thrown down.

Slightly warming the solution increases the strength of the platinum deposit, without, however affecting the colour, and it is, therefore, a useful procedure to adopt in the case of thin negatives, or where very brilliant effects are required.

For normal negatives an old solution, that is, one that has already developed a print, can be used, a little fresh platinum being added to it for each new print. We have found in developing prints 12” X 10”, that if about 3 drams of new developer be added to that just used, good normal results are obtainable. The used solution should not be allowed to remain in the dish, but should be poured into a bottle from which the clear part can be decanted off when required. Of course, in those cases where a number of prints are to be developed at a time, it is simpler to make up a sufficient bulk of solution, and float the prints on it in the usual manner, one after the other. Care, however, must be taken to remove the scum that may form on the surface of the liquid; a slip of paper dragged over the surface, or even a good rocking of the dish, being easy methods of attaining this end.

Needless to say that it will always repay to keep any of the residues of the spent baths, as they will be found to be excessively rich in platinum.

Mercuric chloride may be added to the developer to warm the tone, but owing to the presence of mercury already in the paper, it must only be added with the greatest caution.

In dealing with hard negatives, that is, those having clear shadows and opaque high lights, a flattening of the scale may be obtained by diluting the normal developer or increasing the proportion of the D to the P salt, or, lastly, by using an old and enfeebled developer. There is, however, always the danger to be apprehended of granularity ensuing. We have noticed that the addition of a small quantity of the ordinary platinum chloride of commerce has also an effect in lengthening the scale. A suitable amount will be to make up a new P solution, containing half the chloro-platinite and half the ordinary chloride, instead of the full quantity of chloro-platinite. A curious effect, however, is noticed when the ordinary chloride is used on a print that has been solarized in places. The appearance of this solarization is somewhat the same as in the hot-bath paper, but it shows of a lighter tint on the lemon-yellow ground. When a platinous salt is added to the developer these solarized parts develop out the lighter in tone than the surrounding shadows, with a tendency, sometimes strongly marked, to mealiness; but in the presence of a platinic salt these portions develop out much blacker, and look as if bold washes of Indian ink had been put on the print to emphasize the shadows.

Under-exposed negatives are best treated by slightly increasing the quantity of all the salts, and at the same time slightly warming the developer; but, of course, not much can be done in the direction of compensating for under- exposure, for if a print has not been sufficiently exposed to oxidize the iron salts, it stands to reason that no alteration in the developer can bring about a reduction of the platinum.

In the case of an over-exposed print, something may be done by keeping down the active constituents of the developer, so as to have the action well under control, but the danger of mealiness is always at hand. The best way under these conditions is possible the addition of some other salt that will tend to retard the reduction of the platinum. As we have mentioned above, the use of a platinic instead of platinous salt tends this way, but probably the addition of potassic chloride, as recommended by Willis, will be found more efficacious in the majority of cases. We may also mention that we have found that sodium-chloridethat is, common saltacts very well.The action of a chloride appears to be a true restraining one, and the image simply takes longer to appear, the scale of gradations not being altered in any way. A convenient form of developer for over- exposed prints would be the normal developer having added to it about an equal bulk of a 10 per cent. solution of potassic chloride; but the amount of chloride present appears to make but little difference to the final result.

Most of the errors likely to be met with in this process, and their remedies, will be practically the same as those in the hot-bath process; but there may specially be mentioned the tendency to granulation of the image, which is characteristic of a too short or too feeble development, and the formation on the surface of the print of wavy or streaky blotches from a scum being formed on the surface of a used developer. It may also be mentioned that a general weakness in the tone of the image will, in this process, generally be found to be caused by the amount of platinum salt in the developer having for some cause or other fallen considerable below the normal, and its remedy is self-evident.

The appearance of solarization we have already alluded to, and when caused by negative that usually gives good platinum prints, may be looked for in the fact that the paper was allowed to get damp before printing, or had absorbed moisture in the frame.

WOOD

This process can be applied to wood, both for decorative purposes and for the preparation of blocks for cutting. In the latter case it is undoubtedly this platinum in the bath process that gives the best results, as all the solutions here are applied in as nearly a dry state as is possible, and, therefore, the pores of the wood are not rendered rotten by prolonged immersion or hot solutions. In treating wood, if porous, it should be rubbed over with any size, preferable arrowroot, applied in as dry a state as possible. The sensitizing solutions should also be applied in the same condition, and dried very rapidly. The wood should be developed with as little solution as possible, applied with cotton-wool, and the unaltered image be merely wiped off in the same manner, no fixing with acid being necessary in this case. The image will then be almost entirely on the surface, and the wood will cut freely and not be rotten, nor will the image itself come up as a film under the burin.

CHAPTER VIII.

The Cold-Bath Process of the PlatinotypeCompany.

This process, which in not to be confounded with the platinum-in-the-bath process, is the one which, together with the hot-bath process already fully described, is at the present time in everyday commercial use. The preparation of the paper is, however, as yet a strict secret, and no description of any sort has as yet been published. It differs from the hot-bath process in the fact that it can be developed at the normal temperature of the room. It is true that this can also be done with the hot-bath process, but only as tour de force, and after taking certain precautions, whereas the present process is most successfully worked under these conditions. As we know from the 1888 process, cold development requires increased insolubility of the sensitive coating, and in the present process the insolubility obtained is very remarkable; so much so that prints can be developed in patches, without the lines demarcation showing, whilst bubble marks are unknown. In the 1888 process, insolubility of the coating was obtained by the addition of mercuric chloride to the sensitiser and a phosphate to the developer. In the present process, however, as ordinary oxalate may be used as a developer, the improvement must be sought for in the sensitive coating alone. It may be possible that it is obtained by the use of the bichromates or chrome alum, or some substance tending to make the exposed portions of the image insoluble to a more or less extent. We say to a more or less extent, because the coating of this paper is not in any way completely insoluble; that is to say, if the print be placed in water, nearly all the surface will be dissolved off, and on the application of the developer only a feeble image of a brownish colour will appear. It may also be noted that the insolubility increases with age; that is to say, paper that has been kept for some months, even in an hermetically sealed tube, is more insoluble when old than when new, and paper left overnight in an open drawer will also be found to become more insoluble than paper fresh from the tube. Such behaviour, it may be remarked, is not inconsistent with the presence of a bichromate, and it may be noted that Professor Lainer, who has experimented a good deal with platinum, gives, in the Photographische Correspondez (see Photographic New, 1894, vol. xxxviii. p. 120), the following formula containing bichromate of ammonium for the preparation of platinotype paper suitable for cold development:

Solution No. 1.

Ammonium ferric oxalate	50 grams.
Distilled water 50 c.c.	
Oxalic acid, 10 per cent sol	15 c.c.

Solution No. 2.

Chloro-platinite of potassium	1 part.
Distilled water 5 parts.	

For each sheet of paper mix 8 c.c. of sol. No. 2 with 4 c.c. of No. 1, and * c.c. of a 1 in 25 sol. of bichromate of ammonium.

Lainer notes, however, thatas indeed is to be expectedthe addition of the bichromate reduces the sensitiveness of the paper, and it is not therefore quite proved that a bichromate enters into the composition of this process.

Beyond the advantage of dispensing with the hot developing solutions, this cold-bath paper has another advantage, and that is in the hardness of its sensitive coating, which may indeed be rubbed with considerable vigour without injury. This fact fives us a valuable and useful means of mechanically restraining or retarding the development by the aid of glycerine. To this end the glycerine is actually rubbed, by means of a bit of flannel or pledget of cotton- wool, all over the surface of the picture, or, if preferred, merely over those portions that it may be desired to keep back. The effect of glycerine so applied is very remarkable, in the complete immunity it gives from any marks caused by bubbles or stoppage of the developer, and consequently gives us a very great facility for modifying certain portions of the print. For instance, the shadows in a too heavy foreground may be kept back by glycerining the whole print first, and then applying a developer still further diluted with glycerine, by which means the time of development may be made to extend over several minutes, during which time any of the less-exposed portions of the view can be brought up to full density by the local application of a fresh, strong, or undiluted developer, and that without the slightest danger of the lines of demarcation showing. In the same way vignetting may be most successfully accomplished, as, if the print be well glycerined first, the softest effect in shading off may be obtained by successive washes of developer, getting stronger and stronger, whilst the soft outlines of these washes merge into each other and the white of the background, and allow a vignette to be developed up out of a proof printed in an open frame.

When we add, also, that this paper appears to keep better than the ordinary hot-bath, and indeed for the first month after manufacture actually improves, and when we find that, by a suitable choice of developer, considerable variations in the resulting prints may be obtained, it can be understood how it is that this process has supplanted the old cold-bath process, and, indeed, seems likely eventually to supplant also its only other rival, namely, the hot-bath process.

Practical Working of the Process.

The preliminary operations in this process are exactly the same as those followed in the hot-bath process. The paper, when removed from the hermetically sealed tubes in which it is now sold, should be at once placed in a calcium tube, although it is not so necessary that it should at all times be protected from damp; indeed, for certain effects, it may be purposely exposed to moisture.

In appearance this paper is perhaps slightly more yellow and less orange in tone than the hot-bath paper, but the colour of the image formed by exposure is the same faint purple. The depth to which printing is to be carried on is naturally a difficult matter to describe in words, but it may be said generally that the image is slightly more visible in this process, and therefore printing should be carried on more fully; but this is compensated for by the fact that it is undoubtedly slightly more rapid than the old process. It may also be pointed out that, since development is thoroughly under control, there is but little fear of losing a print through moderate over-exposure, and therefore, if an error is to be made, it should be in this direction.

There appears to be but little difference in the results between prints developed immediately after being taken from the frame, and those which have been kept a week or two, providing, of course, that they have been kept in a proper calcium tube. On the other hand, for certain effects, the print may certainly be kept with advantage in an open drawer over-night, but a prolonged sojourn in a moist place tends to a great flatness and discoloration of the high lights; but on the whole, however, we believe that the best procedure is to keep the prints, an hour or two before development, in an ordinary drawer or box. It is difficult to say absolutely that good does always result therefrom; but, generally speaking, this treatment will tend to give prints of a warmer tone, whilst, as we have already mentioned, there is probably also an increase in their insolubility.

There are two ways of developing this paper. The first way is to float it on a bath containing the developing solution at the normal temperature of the room, in a manner similar to that employed in the hot-bath process. The second is to lay the print face upwards on a table or piece of glass, and brush the developer over it. Both methods have their uses. Where the prints are straightforward and require no dodging, it is undoubtedly the best procedure to float them on the solution, as the brushing on of the developer does very often leave marks in spite of the insolubility of the surface. Mr. Willis himself certainly showed wonderful dexterity in developing paper bit by bit, splashing on the developer here and there, and yet turning out prints without markings, but such tricks are not easy to repeat every time. Bubbles or small marks may not show, but where there are masses of dark shadows, a certain amount of platinum black is dissolved off in the developer, and is apt to run over the whites and so discolour them. At least this has been our experience with most batches of this paper, and it is for this reason that we recommend floating as a rule for ordinary work. At the same time, floating has the drawback that a scum is apt to form on the surface of the bath, which leaves marble-like markings on the print; but this can always be avoided by skimming the developer.

In the case, however, of special prints or work that has to be dodged, or where but one print is to be treated, and it is desired to economize developer, the brushing-on method is most useful. But in this case the face of the print should always be well glycerined first, which will entirely stop any markings from showing. Considerable friction can be used in rubbing on the glycerine without any danger of removing the surface, and, indeed, it can be put on anyhow and in any rough-and-ready manner. The print so treated is then laid, face side upwards, on a sheet of glass or even American cloth, and it is not a bad dodge to slightly glycerine also in places the surface of the glass, as it prevents the paper from slipping. The developer is then applied to the print in almost any way. Perhaps, for straightforward prints, a tuft of cotton-wool, dipped in a normal developer, is the simplest; but the brush, or even the fingers, may be used. Supposing the print to be correctly exposed, the image will at once appear, of a greyish colour in the first place, but rapidly takes a good black as the developer acts. If the action flag, it can always be accelerated by the addition of a little fresh developer. If over-exposure be feared, or if it is required to bring up more of one portion than another, then the normal developer should be diluted with an equal bulk of glycerine; or, if it is desired to have it very much under control, with equal bulks of both water and glycerine. This mixture is applied in the way above mentioned, when the image will come out much more slowly than before. The moment details reveal themselves, some fresh and stronger developer is taken, preferable in a brush, and painted on to those parts that are to be brought up most. Parts so treated will at once attain maximum density, and the stronger developer can then be applied to the other parts at will. In treating a vignette, for instance, the developer would first be applied to the head only, and then this strengthened up gradually, whilst the background is brought out as required.

A stiff hog-hair brush produces a good effect, as it enables all the appearance of a brushed-in background to be introduced; the glycerine makes each successive wash perfectly blend with the next ones, and

no line of demarcation of any sort, not even against the pure white of the paper, can be detected.

Whatever the nature of the print, the moment development is complete to the workers satisfaction, it is placed face downwards in a bath of weak hydrochloric acid and water, and the remainder of the operations are exactly the same as in the case of the hot-bath process, and call for no further comment here.

We have hitherto spoken of the developer generally, as there are two formulae in common use in this process. The first is the old hot-bath developer, that is 130 grains of neutral oxalate of potash to the ounce of water; and the second the D salts already alluded to, and whose composition is given on p. 104, ante. We find, however, from the results of pretty careful experiments, that there is no appreciable difference between prints developed on these diluted developers, or on the same in a condition of saturation, and as it is far easier to prepare and keep saturated solutions, we strongly recommend their use in both cases. Both developers are used cold, that is, at the normal temperature of the room.

Although either developer can be used, still there is a distinct difference between the results obtained by them when both are used normally. The oxalate invariably gives a warmer-toned print than the D salts, with the shadows less dark. The D salts, on the other hand, give a very strong image indeed, with most intense blacks-blacks which, indeed, only reflect as little as 4 per cent. of the light.

These, then, are the general characteristics of the two developers when used normally, but in a paper read before the Camera Club (see Cam. Club Journal, No. 72, p. 119), Mr. Willis gave a list of certain modifications of or additions to them by means of which certain modifications of or additions to them, by means of which certain effects might be produced. We have experimented with nearly all these combinations, and we recapitulate here our deductions therefrom.

Our first set of experiments were in the direction of altering the colour of the prints; that is to say, we tried to get the print of a more or less warm tone. We have already pointed out that the oxalate developer is the most favourable for this, and the more so if the print be not very dry before development. Willis proposed sugar, starch, gum, and such products, as tending to the same end. We have experimented with most of these, but we fail to find any appreciable effect. We have also tried the addition of mercuric bichloride to the developer. We have already alluded to the action of this salt on p. 90, and it is very much the same here. When added in quantities not exceeding half a grain to the ounce of developer, it slightly warms up the tone; but it must be used most circumspectly, or double toning will result.

We have also experimented with both developers used at different temperatures, but beyond the fact that the D salts were always about 2 per cent. behind the oxalate in the blackness of the image given, their behaviour was otherwise similar. We found that the general effect of heating the developer was to give a less steep curve, and should therefore be used in cases of under-exposure, or when too vigorous prints are to be feared. The addition of glycerine to these hot developers had the effect of still more accentuating their characteristics. It may also be mentioned that, although there is no normal developer when used cold, when heated the strong developer will not give the same depth of colour in the shadows that the cold one will.

We have also experimented on the influence of acids and alkalis on the developer, but found no measurable results. If, however, the oxalate developer be very alkaline, it may cause a red discoloration of the print; but, unlike the hot-bath paper, it really does not appear to matter much whether the developer is acid or alkaline, providing, of course, the acidity or alkalinity be not in excess.

Another interesting series of experiments we undertook was that showing the effect of different degrees of dilution of the normal developer. We have already pointed out that there is no appreciable difference between the normal and saturated baths, and very much the same obtains when the dilution is carried on beyond this point, there is always a danger of the image being dissolved off. If glycerine is used instead of water, this is not the case, and the developer may be diluted to almost any extent. Super-dilution of the developer may, however, sometimes be made of practical use. Suppose the case of a negative giving naturally a vigorous print, but from which it was required to get a delicate and soft effect. By taking a very dilute developer, say four parts water, four parts glycerine, and one part strong developer, and, after first glycerining the print, dipping a piece of flannel in this developer and, wringing it out almost dry, and then rubbing over lightly the surface of the print with it, a very delicate image, having no heavy shadows at all, but still showing all detail, will be developed up.

There is, however, another direction in which we desire control over our prints, and that is in the direction of compensation for over-exposure. Several salts have been proposed for this purpose; for instance, the chlorides were stated to have a good retarding effect, but with this kind of paper we have not found this to be the case. The chlorates, it is true, have such an action, but it is far inferior to that of potassium nitrite, the action of which as a restrainer is very remarkable. When added in the proportion of one-tenth of a grain to the ounce of developer, it shortens the scale most considerably, and when increased beyond this the curve becomes almost a vertical line, but at the same time the blacks become very enfeebled. As compensation for over-exposure, or for brightening up prints from thin negatives, probably about one-thirtieth of a grain of the nitrite will be found most generally useful. Its effect, however, on the developer is transient, and fresh should be added as fresh prints are treated. The diagram shows the result of exposing four pieces of the same paper for varying times to the action of light, and developing with different developers. The Curves give the light reflected after development at 60 degrees Fahr., at 170 degrees Fahr., and when one-tenth and one=hundredth of a grain of nitrite are added to the cold developer. The effect of the nitrite, as will be seen, is very marked.

Fig.3.

Lastly, we have tried a few experiments on the results obtained by printing through coloured glasses. Here, contrary to what Willis states, we find that colour makes no difference to the results whatever; and indeed, on looking at the scale of sensitiveness of the iron salts to the spectrum, there is no reason why it should. Of course we were working with clear, colourless negatives. If these were in any way stained, especially yellow, the result then under different- coloured glasses might very well be different.

CHAPTER IX.

The Printing-out Process.

In this process, which was discovered by Captain Pizzighelli, and described by him first in the Phot. Mittheilungen (trans. by Gunther, Photographic News, 1887, p. 124, and Photographic Journal, 1887, p. 17), a visible image in platinum black is formed during exposure in the printing-frame, jest as in an ordinary silver print, and there is no after-development required, as in the ordinary platinum processes, but the unaltered sensitized medium on the paper has merely to be dissolved off by a bath of weak hydrochloric acid, and the picture is complete. On the face of it, this process should be a very valuable one, as, by reason of its simplicity, permanency, and visibility of the printed image, its manipulations should be of the simplest, and when first introduced, it leapt at once into favour, and was put commercially on the market. Unfortunately, however, there was always a great want of certainty in the quality of the results obtained on this paper, at least with the first samples sold, and although of late it has

somewhat improved, its present use is by no means general, and confined, we are afraid, mostly to those workers who want the easiest rather than the best process.

The rationale of the process, and at once the cause both of its success and failure, is the fact first pointed out by Pizzighelli, that by the addition of a suitable developing salt to the sensitizing solution, the iron salt as it is itself deoxidized reduces also the platinum salt. But it must be remembered that this is only the case when moisture is also present in the print. The quantity required, it is true, is very slight, but still it must be there, and this fact alone makes the success of the paper depend on its hygrometric condition. For this reason, in the earlier formulae it was recommended to add glycerine to the sensitizing solution, although this was soon found to be unsuitable and uncertain. It is true that, after a somewhat feeble image has been produced in the printing-frame, this may sometimes be darkened and rendered more vigorous by after-damping the paper, breathing on it or steaming it, and it has also been recommended to develop it on a solution of carbonate of soda. The samples of paper in the market we have always found to vary very much, and it is therefore difficult to make any very accurate statements; but from experiments we have made, we have found no beneficial results whatever from developing either on soda carbonate or oxalate of potash. In no cases did the developer produce any better effect than the simple damping, and even this latter, we may add, in many cases had not the slightest influence on the character of the printed-out image. Cembrano probably gives the true explanation of this when he states that paper exposed and printed quite dry improves by after-damping, but if the paper be exposed damp no improvement is in any case effected by further damping.

But there is also another reason which must always militate against printing out in platinum, and that is the opacity of the platinum image formed, which protects the unaltered salts below it from further light influence, and prevents, unless the exposure be very much prolonged, any further visible reduction, thus making the obtention of vigorous prints a difficult affair.

At the same time, however, sometimes very excellent results are shown on this kind of paper, and as it is essentially an easy process, and the paper itself can easily be prepared by the amateur, we propose to devote a short space to its preparation and manipulations.

In the first place it is, we think, most essential, in order to get good results, that the paper be freshly prepared, as even when kept in a hermetically sealed tube it is very apt to deteriorate. Old paper, however store, should invariably be exposed to the moisture of the atmosphere for some little time before printing, as using the paper quite dry, and relying on it absorbing sufficient moisture after printing to bring out the image, although sometimes successful, is generally very unreliable, and produces many failures, added to which paper printed dry gives weak images, and does not allow the appearance of the image being followed during exposure. Whilst printing in dry weather, however, the growth of the image may sometimes be improved by breathing on it whilst still in the frame; but it is evident that this can only be successfully applied to the whole surface by using a frame having the back in three instead of the usual two divisions. Local parts, however, may often be much improved by breathing on them in this manner.

The most suitable negatives for this process are dense ones, that is, those having a heavy deposit, with clear shadows, and no fog; or, conversely, with normal negatives the process will give a low-toned, soft proof. It is best to print in a very bright light, indeed sunlight is very often the only one that will give good results, and even under these conditions the printing is a long affair, as the paper is very slow indeed. We have in some cases, where we have been endeavouring to get brilliant results, found that the ordinary hot-bath paper exposed alongside for the same time also printed itself out equally well. With the later improvements, however, the rapidity of the paper has certainly been increased; but at its best it must still be regarded as a decidedly slow process.

Printing is carried on in the frame to exactly the depth required, as there is no after-loss in the fixing baths; but the print will sometimes slightly change colour, and lose its blue-black appearance, becoming slightly duller in tone, although not in intensity.

The fixing of these prints is the same as in the ordinary process, and the after-washing and treatment are also in every way similar.

The finished image is, like the hot-bath and the other processes of Willis generally, in metallic platinum, and is, of course, as permanent as these, and prints produced in this manner can be after-intensified and treated in any of the ways already described in a previous chapter for the hot-bath process.

As the best results are undoubtedly obtained on paper that has been quite freshly prepared, and as the preparation presents no difficulty whatever, and can be easily carried out, we append a few of the most successful formulae for its preparation.

Preparation of the Paper.

Any paper that is suitable for the hot-bath process is suitable for this one also, and therefore the chapter dealing with that subject may be consulted again.

As we have mentioned above, the speciality of this process consists in the fact that the developing agent is added to the sensitizing mixture, and in Pizzighellis original description he gives three ways of doing this. In the first one, the paper is first sized, and then the developer and sensitizer are brushed on in one operation; in the second, the developer is added to the sizing mixture, and the paper then sensitized; and in the third, the whole of the ingredients are mixed, and the paper coated in one operation.

We have no hesitation in saying that the first operation will generally be found to be the best and simplest. A coating mixture that contains no sticky size, is more easily and evenly brushed on the paper, and dries as rapidly as is required, whilst the preliminary sizing is always an easy operation, and, indeed, with some papers, will be found to be unnecessary.

As sizes, Pizzighelli recommends gum arabic, starch, and arrowroot, in our opinion the latter being the best, and the gun the worst, as coating is often very difficult on account of its stickiness. There is also a difficulty in getting the gum carefully powdered and dissolved, and every care has to be taken to see that no lumps, however small, are left, as otherwise they will cause streaks and spots.

When arrowroot is used to size the paper in the first place, it should be made pretty strong, about one grain to the dram is a good bath. Even when used with the sensitizing solution, however, it should be about the same strength, depending, of course, on the hardness of the paper, and extent of previous sizing. Gelatine is unsuitable as a size, as it is coagulated by the platinum; therefore papers that have been sized originally with gelatine should be used with great caution, and, if they must be used, it is well to add arrowroot to the sensitive coating, and make it more like an emulsion on the surface of, and distinct from, the paper itself.

The original sensitizing formula of Pizzighelli was composed of ferric oxalate, neutral ammonium or sodium oxalate, and chloro-platinite of potassium; but in his later and improved process (see Photographic News, 1892, p. 293), he recommends the use of ammonio-ferric oxalate and potassium oxalate as giving a more sensitive and brilliant paper.

The following is his latest formula:

A. Chloro-platinite of potassium	10 grams	or 150 grs.
Distilled water	60 c.cm.	or 2 fl. oz.

B. Ammonio-ferric oxalate	40 grams	or 600 grs.
Potassium oxalate, 5% solution	100 c.cm.	or 3 ½ oz.
Glycerine	3 c.cm.	or 1 dr.

Heat the oxalate to about 40 degrees C., and then add the ferric salt, and filter. The solution will keep in the dark, especially if a drop of carbolic acid be added to prevent the growth of mildew.

C. B solution	100 c.cm.	or3 ½ oz.
Chlorate of potash, 5 % solution	8	or1/4 oz.

D. Mercuric chloride	20 grams	or 300 grs.
Potassium oxalate	40 grams	or 600 grs.
Glycerine	2 grams	or dr.

For prints of a black or blue-black colour take

A.	5 c.cm.	or 77 fl. grains
B.	6 c.cm	or 92 fl. grains
C.	2 c.cm	or 30 fl. grains

The above, making 13 c.cm. or 3 ½ drams, should give about enough of the mixture to cover a sheet of paper 26 X 20 inches.

The chlorate of potash solution C plays here the same role as in the ordinary hot-bath process, that is to say, for hard negatives its quantity should be reduced, and for soft negatives, of course, increased.

The D solution is for the purpose of obtaining prints of a warm brown tone, and the following may be taken as an average formula, which may be altered slightly in either direction to suit particular cases:

A.	5 c.cm.	or	1 dram.
C.	4 c.cm or	1dram	
D.	4 c.cm or	1 dram	

The amount of chlorate of potash may, of course, be also varied in this formula to suit the negative or desired result.

It will be noted that in the above formula the use of glycerine is advocated in order to provide a hygroscopic substance that will keep the paper to the proper degree of moisture; but we think that its use in our damp climate, if not entirely suspended, should only be undertaken with great caution and in the driest weather.

For the coating and drying of the paper, we can only refer readers to the method described for the hot-bath process.

Pizzighellis process has been considerably worked in Germany and Austria, and sometimes with very fair success, and we append, therefore, a few further formulae of some of the best-known workers.

Wischeropp (Photographic News, 1891, p. 39) gives the following simplification of Pizzighellis formula:

A. Sodio-ferric oxalate*	40 gram	or 600 grs.
Sodium oxalate neutral, 3%solution	100 c.cm.	or 3 fl.ozs
Potassium chlorate	1 gram	or 15 grs.
B. Distilled water	60 c.cm.	or 2 fl.ozs
Chloro-platinite of potassium	10 gram	or150 grs.

Mix 8 c.cm. of A, 5 c.cm of B, for each sheet of paper 26 X 20 inches.

To obtain warm tones, chloride of mercury may be added to the above. A normal formula would be about 1/15 of a gram of the salt to each 13 c.cm. of the mixture given above.

Krause recommends, and with reason, the rapid drying of paper coated with any of the above formulae, and uses a little tin oven, warmed by means of a spirit-lamp, for the purpose. Rapid drying, in order to obtain brilliant effects, is as essential in this process as in the ordinary hot-bath one, and, therefore, our previous remarks on the subject should be re-read here.

The preparation of printing-out papers does not seem to have been much practised in this country, and but few workers have recorded their experiments. Mr. Cembrano (see Camera Club Journal, vol. ii. p. 155) publishes the following experiments: He notes that the potassic- gave him better results than the sodic oxalate. His best results were obtained by using Pizzighellis third formula, where the gum arabic was mixed with the sensitizing solution; but he agrees that it is generally best to employ paper that is already sized. The following is the formula successfully used by this gentleman:

A. Potassium chloro-platinite	1 in 8 solution.
B. Sodio-oxalate, 3% solution	8 drams.
Sodio-ferric oxalate	3 drams
Gum arabic	2 drams

Warm the oxalate and dissolve the iron therein, then add the gum, dissolve well, and then strain.

C. Solution B	2 drams.
Pot. chlorate, 5%solution	10 minims.

To sensitize a sheet 26 X 20 inches take

B	90 minims.
C	30 minims
A	2 minims

Cembrane notes the slow printing qualities of this paper, and tried to improve it in various ways. He notices a slight acceleration due to the addition of a hygroscopic substance such as calcium chloride; the actual amount he found best was an addition of 4 grains to each sheet of paper coated. Mr. Wellington, in the same journal, mentions that he had obtained good results by adding sugar to the gum solution, and it is quite probable that this may be found to be a useful addition, tending perhaps to improve the tone or colour of the image.

CHAPTER X.

Platinum Toning.

Although, generally speaking, there is no difference in the chemical action that takes place when a silver salt is used instead of an iron one for the formation of a preliminary image to be replaced by platinum, still, in photographic parlance, a distinction is made, and the term platinum toning is used to denote the process whereby a preliminary image, printed out or developed, is first obtained in silver and then the silver of this image is by an after-operation replaced to a more or less extent by platinum.

Many varied formulae for platinum toning are to be found, but as they are all only modifications of the original process of Mr. Lyonel Clark, we shall proceed first to describe this process, adding to it any modifications of later date that we have found useful.

Platinum toning is applicable, with certain modifications, to probably every silver printing process that exists, but the best results are perhaps obtained on matt surface chloride of silver paper, in which the silver is present in large quantity so as to give a vigorous image.

Such paper is now a common article of commerce, or can be easily prepared. The most suitable negatives are plucky ones with full gradation, and the paper should be printed out until the highest lights are slightly degraded, and the darkest shadows should be distinctly solarized or bronzed. Paper may be toned at once or kept before toning. It should preferable be washed in several changes of water before toning, until the milkiness caused by free chloride of silver ceases. Paper can, however, be toned without washing, but the chloride carried over soon dirties and destroys the toning bath. The following bath will tone prints very rapidly, that is, in a few seconds, the red colour of the print rapidly giving way to platinum black:

A. Stock Solution.

Chloro-platinite of potassium	60 grains.
Distilled water up to	2 fl.ounces.

Toning bath: 1 dram of stock solution A, made up with water to 2 fl. ounces, to which is added 2 or 3 drops of nitric acid.

In cold weather, or if prints tone slowly, this bath may be slightly warmed. A simple way is to float the prints on this bath one at a time, and pick them up and examine them in the hand. They should be refloated, if necessary, until all trace of reddishness, viewed by transmitted light, disappears. The resulting colour will then be of a rich purple-black or pure black, depending on the original tone of the print; for instance, ammonio-nitrate prints will give, if vigorous, very black tones, whereas ordinary chloride paper, if red when placed in the platinum, will turn a plum-black, or, if the image be thin, of a greyish-black colour. The prints being wet when placed on the bath, no bubbles or marks are to be apprehended, and, if preferred, prints may very well be toned with a brush or pledget of cotton-wool.

Warmer tones, that is, those having a brownish-black tendency, may be produced by diluting the above bath with four or five times its bulk of water. The effect of this is to keep the toning action under control, and it can, therefore, be stopped whilst there is still some of the silver salt left unconverted, which, mixing with the platinum black, gives a warmer tone to the image.

Fixing is done in the usual manner, but owing to the fact that the toning bath is in acid state, it is advisable, in order to prevent sulphur being thrown down in the fixing bath, and sulphur toning of the print setting in, to wash the prints, before placing them in the hypo, in water, or a bath of water rendered slightly alkaline may be used. The subsequent washing of the prints in order to free them of all hypo, has to be carried out as thoroughly as in the case of a gold-toned print.

Clark notes that no difference in the gradation of the image is effected by altering the strength of the toning bath, that is, a hard print will always be a hard print, or vice versa, whatever the dilution of the bath, within limits. These he places as between 1 part of the chloro-platinite in 15 parts of water as a maximum strength, and 1 in 3000 as a minimum. Outside these limits in either direction there is a tendency to render the fine detail of the image of a yellowish colour. He also notes that no toning takes place unless the bath be in a distinctly acid condition.

Clark also made experiments to determine the permanency of such prints. He points out that the platinum and silver will form an alloy together which has not the stability of platinum, being, indeed, soluble in nitric acid. This process, therefore, is not so stable as the ordinary platinotype processes proper; but, at the same time, the results of several test with powerful oxidizing agents showed that its permanency is superior to that of prints toned with gold in the ordinary way.

Many variations of the above toning bath have been proposed from time to time, and, like gold toning, almost any combination may be used, providing the bath be acid. Mercier (Bull. Soc. Franc., vi., 2, 194) recommends the following bath:

Chloro-platinite of potassium	1 to 2 parts.
Phosphoric acid (pure)	5 parts
Water	1000 parts

Mercier gives also a formula for use with the ordinary platinic chloride of commerce, by means of which it is converted to the platinous stage, and the great loss in intensity in the image which always obtains when the ordinary chloride is used, is obviated:

Platinum chloride	2 parts.
Neutral oxalate of potash	.6 part. [note decimal]
Water	100 parts.

This solution is exposed to light until the colour changes to a ruby red and no precipitate is formed on the addition of a drop or two of a saturated solution of chloride of ammonium. The action is rapid in summer, but slow in winter. The bath is made up for use to a bulk of 1000 parts by the addition of water.

Burton (Photographic News) proposes another useful variation as follows:

Chloro-platinite of potassium	2 grains.
Citric acid	5 grains
Common salt	8 grains
Water up to	1 ounce.

It may be noted, generally, that the use of a mild organic acid is preferable to that of nitric acid where the surface of the print is in gelatine, as the latter acid has a tendency to cause stains on this medium. The addition of salt in Burtons formula is probably made in order to ensure the conversion of any free nitrate of silver on the print into the visible milky-white chloride.

It follows that the last-mentioned bath may be used very advantageously with that class of papers that embraces both the developable and printing-out gelatino-chlorides and bromides of silver, or the following bath as originally given by Clark, and also by Stieglitz (Amateur Photographer), may be also successfully used:

D.* Oxalate of potash neutral	5 ounces.
Mono-potassic orthophosphate	3 ounces
Water up to	50 ounces

P. Chloro-platinite of potassium	60 grains.
Water up to	2 ounces.

The toning bath consists of 3 parts of either of the D solutions, 1 part of P, and 2 parts of water. All the operations in connection with these papers are the same as those already described.

Toning With Other Metals of the Platinum Group.

We except gold from this category, as its use is so well known in photography, but a few notes on the results obtainable by the rarer of the noble metals may be useful.

Palladium.Clark (Camera Club Journal, vol. iv. p. 202) used a chloro-palladite of potassium for toning ordinary silver citrate and chloride prints, the strength of the solution being the same as when platinum was used. He notes that it tends to give images of a somewhat greeny-brown colour. Prints toned with palladium and afterwards intensified with silver gave very pure sepia tones.

Iridium.

Mercier (ante, p. 138) gives the following bath for iridium toning, by which the results obtained are of a violet colour:

Tartrate of sodium	0.15 part.
Double chloride of iridium and sodium	1.5 part
Water	1000 parts.

The above bath is boiled, and 400 parts of water and 10 parts of acetic acid are added; when cold it is ready for use.

Osmium.Mercier gives the following bath:

Yellow chloride of (Fremys) ammoniacal	1 part.
Chlorate of sodium	04 part
Succinate of sodium	4 parts.
Water	1000 part

The prints change first to a burnt sienna colour, and, if toning be continued, to a bright blue, which does not appear to alter in the subsequent fixing bath. Mercier also notes that if mineral acids be added to this toning bath, the resulting colour is a violet, but in this case it is advisable to add sulphite of soda to the fixing bath.

Rhodium.Mercier notes some experiments with this salt, but states that in no case was he successful..

It may be noted, generally, that prints that have been toned with iridium or osmium are capable of being toned again with gold, so that a further variety of colours is obtainable.

CHAPTER XI.

Direct Enlargements in Platinum Paper.

The platinum process has, as a rule, been devoted to the production of prints by contact, but some years ago, in America, and also at the present time, enlargements have been made direct on the paper by means of the electric light. In a paper read before the Camera Club, one of us showed examples of enlargements made by himself, with an arc electric light of about 1100 candle power. This electric light is of but small power compared with that which can be obtained, as it consumed only about 1100 watts of electricity. The apparatus required for this light is very limited, where the enlargement required is not more than nine times the area, and every photographer who has a direct current of electricity at his command, is in a position to avail himself of it. It is proposed in this chapter to describe the apparatus and the methods of adjustment when using the electric light of this dimension, and also with solar light.

We will suppose that we are limiting ourselves to the enlargement of a quarter-plate of twice linear.

In the first place we must have two condensers, preferably plano-convex, sufficient in diameter for our purpose, and it is convenient that they should be about nine inches focal length each. They can be obtained very cheaply, of cast glass, and there is no great precaution necessary to take in selecting them, beyond seeing that they are fairly free from bubbles; if many bubbles are present the print is apt to show images of them, though, by keeping the negative a little way from the lens, they can be made to disappear. We can find the necessary diameter of the condensers by taking the length of the diagonal of the quarter-plate to the diameter of the condenser. It is a little over five inches, but it is convenient to allow an extra inch, which will make them six inches in diameter. This allows the negative to be in the cone of rays even when some distance from either one of them, a very necessary point, as we shall see when focussing. A convenient way of setting up the apparatus is as follows: The condensers are mounted in two firm wooden-framed stands, with a device enabling their heights to be altered at pleasure. Their centres are so adjusted (Fig. 4). One of the condensers, C2, is placed in front of the electric light, E, with its plane side towards it in such a position that its axis passes through the electric arc. The distance of this lens is guided by its focal length. The arc should be placed just within its focal distance, so that it throws a circle of light, a little bit larger than the diameter of the lens, on a screen placed about twelve inches from it. In this disc of light the second condenser, C1, is placed, and it should throw a cone of rays coming to an approximate focus of about seven inches from it. In this case the plane side of the condenser is away from the light. A photographic lens of some seven and a half inches focus, and which has a fairly flat field, is then, without any stop being inserted, held in a perfectly rigid camera front, or in a clamp, and so placed that the focus of the rays, coming from the condenser, falls within its front combination. The negative, N, to be enlarged is then inserted in a proper holder in front of the second condenser in such a manner that the image, when sharp, is of the required size on a board, S, to which a sheet of white paper has been pinned. It frequently happens that a circle of orange and blue light is seen cutting the picture, this shows

Fig. 4.

that the adjustments are not accurate. If the coloured circle cuts the corners of the picture uniformly, it must be got rid of by moving the lens backwards till a clear circular white disc of the necessary size is obtained, and the negative must be moved backwards or forwards from the condenser, till a sharp image is again secured. Patches of blue are due to the light from the arc in contradistinction to that of the poles. The positive pole of the electric light should be the top pole, and be thrown a little behind the bottom or negative pole, and the current should be sufficiently strong to allow the white-hot crater of the positive pole to be clear of the latter, for it is this crater which creates the most photographically active light. When patches of blue light are seen they indicate that this position of the crater has not been secured. That the most photographically active light proceeds from the crater is easily proved by throwing an image of the poles on a piece of chloride paper by means of a lens, when it will be found that the image of the crater blackens the paper much more rapidly than that of any other portion of the luminous image.

When the focus of the image is correct, platinum paper is placed on the focussing paper, and the exposure is given. With an electric light of about 1100 candles, the time for exposure for a thinnish negative will be from about 15 to 25 minutes. With a denser negative it will, of course, be longer; but it rarely happens that any negative will take more than an hour to print. For the purposes of enlargement the deepest shadows of the negative should be as nearly bare glass as possible, and any yellowness should be avoided. It should be remarked that the density of the negative, to give a good enlargement, may be less than that required for a contact print; in fact, a rather feeble negative, if very bright, will give the best results. It is a good precaution to place a sheet of glass between the electric light and C2.

When sunlight is used, very much the same procedure is carried out; but the condenser C2, next the electric light, need not always be used, if the photographic lens employed is exactly the proper focus. A large looking-glass, M, is employed to reflect the light on to the condenser next to the lens, and care is taken that the focus of the beam of the condenser falls within the lens; so long as it does not travel outside, it does not matter if it is not always quite central. Supposing the lens to be of slightly too long or too short a focal length for the image (Fig. 5) of the necessary size, the focus of the condenser lying either too near or too far from the photographic lens, L, to give a proper illumination of the field where the size is correct, then the use of the second condenser, C2, becomes necessary. In Fig. 5 it will be seen that the position of F1, the focus of C2, can be caused to recede or approach C1. The further F1 is from it, the shorter will be the focus of C1, and the closer it is (of course, within limits), the longer will be the focus. Hence C1 is placed at such a distance from the condenser (behind which is the negative, N), the focus of the latter being altered to the necessary extent, that it falls exactly on the photographic objective. The great point to observe is that the centres of the condensers be on the same axis. To secure this the objective is removed, and the mirror turned so that light coming through the aperture cut for the lens, occupies the centre of the focussing screen. The first lens is then approximately focussed, the small patch of light formed being also in the centre of the screen. The second condenser is then placed in position to five the same result, after which the photographic objective is replaced. The negative is then put in position, the image focussed to the proper size, and the back

Fig. 5.

condenser moved parallel to its position till a uniformly lighted field is secured.

The printing with a bright sun is quicker than with the electric light, and a good print may often be obtained in ten minutes, or even less.This will be understood when it is considered that the light which falls on the negative is simply spread out to fall on the area of the enlargement. There is no loss of light by reflection and absorption, and it may be concluded that the exposure is about three times that which calculation would give. Suppose a negative has to be enlarged twice linear, and that a contact print can be obtained in one minute, then it will take twelve minutes to make the enlargement. There is nothing peculiar in manipulating the paper; the great point is that it should be flat, and it is well to leave it ten minutes lying on a table in the room where the enlargement is to be made, before pinning it in position, so that it may posses the same moisture as the air in which it has to be exposed. Arrangements should be made to prevent diffused light reaching it during exposure, and very obvious precautions should be taken to effect this. The prints produced are, as a rule, more even than the contact prints, for the margins of the print receive slightly less exposure than the centres, and, as of necessity, the margins of a negative are slightly less dense than its centre, on account of the want of perfectly equal illumination of the field, a compensation is made in the camera prints.

A small calculation will show the relative values of the printing powers of sunlight and the electric light. Sunlight has the same value, optically, as 5000 candles when placed one foot off the screen. The electric light used has the value of 1100 candles. Hence, the value of sunlight is about 4 times that of the electric light, when placed one foot off. All we have to do is to compare the values of the two sources when falling on the condenser, which is next the photographic lens. If the light be six inches from the first condenser, evidently four times as much light will fall on it as would be the case if it were one foot off, but the area of the disc of light in which the second condenser is placed is at least eight inches in diameter. As the first condenser is six inches in diameter, the light on the second condenser is, therefore, only or (say half) of that falling on the first. Had it all fallen on it, it would have been equal to 4400 candles, but owing to the increased disc, it is only equal to 2200 candles, and as the photographically active rays in sunlight are about 1.3 times greater than that of the electric light, it follows that the 2200 must be divided by 1.3, or the value of the light formed. The intensity of the electric light compared with that of the sun is as 1700 to 5000, that is, the latter will print three times more quickly than the former, always supposing the sunlight is that near midday and from an unclouded sun with a dark sky. It may be of interest to note the fact that the different thicknesses of glass cut off approximately the same amount of the photographically active rays. Roughly, it may be said that of these rays reachthe plate, the different amounts of surface reflection due to the varying curvature of the glass, probably making up for the different absorptions.

CHAPTER XII.

Spectrum Sensitiveness, Gradation, and Rapidity Of Platinotype.

It is a matter of practical interest to know the rays of light to which platinotype is sensitive, since the relative rapidities of printing in winter and summer are in question. It must be recollected that in the winter, owing to the low altitude of the sun above the horizon, the blue rays are very much diminished, owing to the scattering by the fine atmospheric particles which intervene between it and the paper. It is, therefore, a point in favour of any printing process that it should be as sensitive as possible to the green rays, and, if possible, to the yellow and red rays. It has been said that the blue rays are diminished in winter, but a little more explanation, perhaps, may be required to make the matter plainer, for the same applies not only to winter printing, but to printing carried out at different times of the day. Supposing the different component and coloured rays of the light of the sun were unity when it was outside our atmosphere, then the following would be the reduction of the different rays when the sun gradually approached the horizon:

Sun being above the horizon. Colour. Wave Leng. 90o 30o 19o 14o 11o 9o 8o7o Just 30 30 30 30 30 30 at 1 2 3 4 5 678sunset

Red © 6562 .912 .832 .759 .693 .632 .576 .526 .480 .019 Orange (D) 5892 .868 .754 .655 .569 .494 .428 .372 .323 .001 Green (E) 5269 .803 .644 .518 .427 .334 .268 .216 .173 Blue (F)4861 .738 .544 .402 .296 .219 .161 .119 .088 Violet (G) 4307 .609 .367 .220 .137 .084 .051 .031 .0199 Limit of Violet (II)3968 .506 .254 .128 .071 .033 .016 .031 .004

This table shows that the violet light decreases enormously as the sun travels towards the horizon.

When platinum paper is exposed to the sunlight-spectrum, it is found that the maximum sensitiveness is close to F. In Fig. 5 are the results of a careful measure of a print taken by exposing platinotype paper to the spectrum. The sunlight was in a bright June day near noon. It will be seen that the paper is sensitive almost into the orange. Now, ordinary chloride of silver, as found in albumenized paper, is very much less so, and has its maximum of sensitiveness nearer the line II, or the boundary point between the ultra-violet and the violet. We may for our purposes take the maximum of the one at G, and of the other at H, as the position that governs the comparative sensitiveness of the two at different altitudes of the sun. If we compare the sensitiveness of the two at 30o and 14o30 above the horizon, we shall see that, whilst the loss for platinotype would be only from .367 to .137, or from 1 to .37, the loss for chloride would be from .254 to .071, or from 1 to 27. From this fact we have a good example of the increased general sensitiveness of the one in winter time over the other. The same applies, of course, equally in other seasons for different times of the day. There is, therefore, on this score alone, an advantage in the use of platinotype.

The next point to be taken into consideration, is the gradation given by platinotype in comparison with silver prints. The annexed diagram illustrates the difference between the two. The intensities of the light acting in the two cases were the same, and varied from 1 to 1/256 parts. It will be noticed that platinotype was practically black when only 1/8 of the whole exposure had been given, and was white at 1/256; whilst the toned silver print was only black when the full exposure had been given, and was practically

Fig. 7.Intensities of light-acting.

white when 1/64 had been given. The straight sloping lines show the general gradation of the two, and it does not differ much in either as indicated by the angle of the slope of these lines. It appears from this diagram, that with a plucky negative, platinotype would give the best result, but with a thin negative, on account of the greater gradation in the parts of a print which are nearly white, the silver print would give the better print. The question of rapidity is also practically settled by these measures, as far as these two specimens of platinum and silvered paper are concerned.

There is, however, a power of altering the gradation of prints in the preparation of the platinum paper, as Dr. Eder and Pizzighelli have shown. The addition of oxidizing agents to the iron salt produces a marked effect, as also does the heat the strength and temperature of the solution of oxalate used in development.

APPENDIX

The Use of Other Salts Than Platinum for the Formation of the Finished Image.

It my be remembered that in Mr. Williss specifications (p.20) the use of other metals than platinum for the formation of a visible image is claimed, amongst which are palladium, iridium, and gold; it is therefore necessary to examine the behaviour of these metals.

As regards their use in the hot-bath process, Pizzighelli has experimented with them, and we have ourselves added to these results by undertaking a series of trials with these different metals, applied to paper prepared for the platinum in the bath process.

In the hot process, palladium is substituted for platinum with complete success. From the great similarity of the chemical behaviour of these salts with those of silver and platinum, it was to be expected that it would do so, but its great expense hardly brings its use into the range of practicability. The resultant colour of photographs taken with palladious chloride is of a sepia-brown colour, but they are very subject to solarizationthat is to say, the parts that have received the most exposure develop out lighter than the half-tones; this phenomenon is also observable in platinum prints, but in a less degree. Palladium prints also possess the property of being capable of being toned by gold chloride, by which treatment they assume a violet colour, and, at the same time, the effects of solarization disappear.

If the palladious and platinous chlorides be mixed, the resultant colour partakes of the nature of the combined salts being brownish black or blackish brown, as one or other of the salts prevails in its action. The brown colour that can be obtained by the use of palladium would no doubt be a useful ally in the hands of the artist, but the Platinotype Company prepare a special paper (sepia paper), by means of which the same results are obtainable.

Iridium, although also one of the platinum groups of metals, behaves differently from the others under the action of reducers. Although its compounds resemble in their action those of platinum, they have also considerable resemblance with those of iron, and Pizzighelli states distinctly that their use is not practicable, it being impossible to develop the iridium image by the same agents as would a platinum one.

Gold.

The compounds of gold are, with the exception of the hyposulphite, all reducible by oxalate solutions when cold, and even the hyposulphite does not withstand the action of hot oxalate; on this account gold also is not a feasible agent of which to form the positive image, as it could be reduced on the high lights as well as on the shadows.

The Use of the Above Salts in the Cold Process.

In this process there is considerable difference in the chemical action, as we have on the paper simply a metallic image, and we can therefore present to it the salt of any other metal simply in an aqueous solution of the terchloride be applied, it is at once thrown down without the addition of any other substance as a developer. The colour assumed by the print is a purplish blue, almost a slate, but unfortunately the result is marred by a very slight reduction of gold that also takes place over the high lights. The gold here is thrown down in the pinky state, and, to portraits, gives almost a natural colour to the high lights of the flesh.

The above process is almost identical with the chrysotype process of Sir John Herschel, the only difference being in the salt of iron used to form the provisional image, the ferrous oxalate being substituted for the ammonio-citrate of iron of this worker.

At the same time, we remarked that the gold is much more easily reduced than the platinumthat is to say, that less exposure is required. Thinking, therefore, that an addition of gold to the platinum might act as an accelerator, we tried a mixture of these two salts; unfortunately the result was negative, as the two react mutually on each other, and a copious black precipitate is thrown down.

Palladium in the form of the chloro-palladite of sodium acts well in the place of the platinum salt. Its behaviour is the same as in the hot-bath process.

Hot Bath. Further Formula.

Lainer (Photographische Correspondenz, vol.xxx. p. 17) gives the following formula for preparing hot-bath paper. He uses the following solutions. A. Normal ferric-oxalate solution (see formula, p. 58, ante). B. Iron chlorate solution, prepared by adding 8 parts of a 1 in 20 solution of oxalate of potash to every 100 parts of the normal iron solution A. C. Platinum solution made up of 1 part of chloro-platinite of potassium dissolved in 6 parts of water.

To suit negatives of different qualities the proportions are tabulated hereunder:

HardBrilliantNormalWeak negatives.

A 5.5 4.5 3.5 to 2.51.5 B -1 2 to 34 to 5.5 C 6 6 66 Water 1 1 11

Ganichot (see Bull. Soc. Francaise de Photographic, vol. viii., N.S., p. 458) gives a formula for the preparation of platinum paper with the sodio instead of the potassio salt of platinum, which he claims not to suffer from damp. He prepares the following solutions:

A. Anhydrous iron perchloride ... 125 grams. Water .... 1000 c.cm.

The solution is filtered, and ammonia added drop by drop, until no further precipitate is formed. The precipitate is a hydrated peroxide of iron. This is filtered and washed.

B. Oxalic acid ....50 grams. Water .... 150 c.cm.

This solution is boiled, and A solution in its moist state is added. The resultant is filtered and 2.50 grams of chloro- platinite of sodium is added, and the solution made up to 250 c.cm. with water. Sized paper is coated with this solution and rapidly dried. It is printed from in the usual way, and developed on the following bath at ordinary temperatures.

Oxalic acid ....28 grams. Chloro-platinite of sodium ...... 2.5 Water .... 250 c.cm.

This process, it may be noted, partakes of the character of the hot-bath, cold-bath, and printing-out processes.

Advanced Development of the Hot-bath Process.

In a preceding chapter we have dwelt very fully on the ordinary manipulations to be carried out in working the hot- bath process in what may be called the ordinary way, but, as in other processes, there are special treatments which can be adopted for certain cases, constituting what one may call the higher possibilities of the process. Great latitude in treatment is undoubtedly to be met with in the ordinary hot- bath process, and this is more the case with the present brands of paper than with the older ones. We have, therefore, thought it advisable to resume, under the present heading, an account of what may almost be termed tricks that can be played with this brand of paper.

In the first case, in regard to keeping the paper dry. This is certainly a most wise and necessary provision, but still, by an intentional damping, certain effects may be produced even with the ordinary hot paper. For instance, damping hot-bath paper, preferably after exposure, affects its qualities in two ways. It lengthens the scale of the paper, and makes it, therefore, more suitable for printing from dense negatives, and it also warms the colour, making it a brown- instead of a blue-black.

In order to get the fullest effects out of paper so damped, it will be advisable to work the developing solution at a temperature not higher than about 90o F., to use the D salts instead of the plain oxalate, and, further, to strongly acidify the bath with oxalic acid. If warm tones are desired as well as a lengthened scale, a diluted oxalate bath can be used instead of the D salts, as these latter, at least in normal prints, have a tendency to keep the colour of the print cold. In the event of the oxalate being used, it should be diluted, potassium chloride added, and the proof be fully, and, indeed, over-printed. The following would be an approximation of a suitable bath: Two parts normal oxalate solution, two parts water, one part oxalic acid, and one- twentieth part potassium chloride. Development will be slow and under control. It may also be noted that paper that has been kept is more amenable to this treatment than new paper.

If the D salts are used, they should be of normal strength (1/2 pound of the mixed salts in 50 ounces of water), and not be acidified. Generally speaking, the d salts will always give a slower development than the oxalate, and, therefore, dilution is not so necessary to get development under control.

To get flat prints, that is, those having but few gradations, if oxalate is used the solution should be strongly acidified with oxalic acid. The acid may be added almost until the bioxalate begins to be precipitated. This development will give an image in which the half-tones and shadows are weak, if the paper be dry. If the D salts are used, they should be acidified, and of normal strength. This is probably a better developer for weak negatives than the last, as the shadows are not weakened in intensity, but only the scale is shortened. Although we give these methods of dealing with weak negatives with a cold development, which are due to Mr. Williss experiments. still we are of the opinion that the hot development is the best in this case, but it is interesting to notice the action under all circumstances. We may also sum up the characteristics of the D salts when used for ordinary hot-bath paper, but at a low temperature, so as to be under control, for which we are indebted to the researches of Mr. Willis.