of clay is put into an iron box at the end of apparatus which is about 3 ft. in length, 2 ft. in width and about 18 in. in height. Across the front end of box is a piece of wire netting, 24 meshes to the inch, through which the material is forced. The clay is pressed through the meshes by means of a movable plate or ram. Connected to the back of the plate are two square iron bars, the under sides of which are slotted. These bars pass over two gearing wheels underneath, which when the machine is in motion forces the ram ahead, which in turn presses the clay through the meshes of the netting. The box or machine empties itself in about two minutes. The material is then taken up and weighed out into 2 and 7 lb. pieces to be formed into pipkins. The next operation is forming. A piece of clay is placed on a circular wooden block about 14 in. in diameter, attached to the under side of which is an upright shaft. This shaft connects itself below to a 3 ft. drive wheel with a treadle attachment. The operator, to make the circular block with the ball of clay revolve, forces the treadle back and forth with one of his feet, causing the block to revolve at any rate of speed. The pipkin is formed entirely by the hands, the attendant pressing into the center of the ball of clay, which by holding the hand in a certain position causes it to grow in height, thickness and in a circular shape, the point of the gauge showing the attendant when

two compartments, the upper one for drying purposes and the lower one for burning. It is called a down draught kiln, having an 18 in. square chimney running up through the center. Each compartment has a convex crown 9 in. in thickness. The lower kiln is about 10 ft. in height and the upper about 8 ft. The lower kiln is fitted up with seven 6 x 18 in. fire bags. After the lower kiln is loaded up with about 1,800 pipkins, the doorway is plastered up and the fires started. The flames from the fire pits rise up through the bags on the inside to the crown above and down to the bottom of the kiln, where they pass through eight holes in the bottom corners of the chimney, passing out at the upper end. After burning for about twenty-four hours at a white heat, the fires are then put out and the kiln allowed to cool. After cooling, the pipkins are taken out and packed for market. The clay is bought by the ton, the price varying from \$1.50 to \$5 per ton, according to the grade.

Our sketches were made in the establishment of John J. Leonard, West Bergen, N. J.

SOME RECENT ADVANCES IN PHOTOGRAPHIC CHEMISTRY.*

By CHAPMAN JONES.

PHOTOGRAPHY, as ordinarily practiced, is an em-

usual in other industries, seek the advice of those who are able to give them assistance.

As an example of the disastrous effects of working in the dark, I may say that I have heard of photographers, both amateur and professional, who have many large and valuable negatives intensified by the mercury and silver cyanide process that have so much changed from their original condition as to cause grave anxiety. It would have been wise, though perhaps hardly possible, if photographers had declined to use this process until it had been properly investigated by a chemist. Then no trouble would have ensued.

We may for convenience sake, with reference to the majority of photographic operations, divide the photographer's work into two parts, namely, the making of the negative and the making of the print. If we accept those cases in which, for scientific purposes, the negative itself is preserved as the record, as, for example, in spectrum work, then the end and aim of the photographer is the preparation of the print, and the negative is nothing more than the tool used in its production. In this sense, therefore, the print is of much more importance than the negative. It should be of a permanent character, while the tool used in the making of it may perfectly serve its purpose, though it were so shortlived as to fade away immediately after it had yielded the print. But it is convenient, and often of

MANUFACTURE OF PIPKINS.

the required size is reached. A good operator can form from 18 to 50 pipkins per day, according to size, which run from ½ pint to 1 gallon. After forming they are put into the upper part of a kiln to dry. As soon as they can be handled they are glazed. This requires three operations, the first two being on the inside and the other on the outside. The first process is a white body mixture, consisting of a solution of felspar, flint, china clay and ball clay. The second process consists of the same ingredients, with the exception of ball clay, with addition of zinc, Paris white, and dry white lead, the materials being mixed up with water and run through a 120 mesh sieve. The pipkin is held in one hand and the solution poured into it with the other. After the inside is thoroughly saturated the solution is poured out and the pipkin put one side to dry, which takes about 4 or 5 hours, the coating drying white. They then pass through the next operation on the outside, which is done by dipping, the attendant spreading his hand out on the inside of the pipkin and pressing it down into a mixture called black lining or Albany slip. An operator can glaze from 1,200 to 1,500 per day. After they can be handled they are placed in the lower part of kiln to burn. The kiln is about 30 ft. in height, 12 ft. in diameter, 2 ft. in thickness at the bottom and made of brick. It is divided into

pirical art. Although it is founded upon, and intimately connected with, certain branches of chemistry and optics, very few photographers know anything of these sciences. The ordinary practitioner, whether amateur or professional, works entirely by rule of thumb, and is guided by tradition rather than by reason. It is natural, and perhaps necessary, that this should have been so at first, but it must be allowed that the sooner the art is put upon a sure foundation the better, though doubtless there will always remain some who will prefer the old ways.

There is now a larger amount of scientific work being done in connection with photography than heretofore, and I would suggest that the time has come when we should make a determined effort to get rid of uncertain and obscure processes in serious work. When one's only aim is amusement, then, of course, there must remain free liberty to follow any fancy, but for the production of valuable records of any sort, whether pictorial or otherwise, I think the time has come when photographers ought to avail themselves to the fullest extent of all the scientific knowledge at their disposal. Any who are unable to guide themselves should, as is

great importance from an industrial point of view, that the negative shall be stable. And if the negative is not right, the print must be wrong, and if the negative is produced by uncertain processes, we never can tell what the print will be. The science of negative making becomes therefore, I think, of as much importance as the science of printing processes. As the chemistry of these latter has received enough attention to enable any one to make prints that are perfect from a chemical point of view, while the chemistry of negative making has been very largely neglected, I have spent a good deal of time during the last few years in examining some of the operations in common use, and propose this evening to look at one or two matters in connection with the chemistry of negative making on gelatine plates.

The silver bromide particles held in the gelatine film are so changed by suitable exposure to light that the developer is able to take away the bromine from them. In a chemically perfect negative, after fixing and washing, the image will consist of pure metallic silver, and it does not matter at all where the bromine has gone or what changes it has produced in the developer, so long as no trace of it, or what it leads to, remains behind. But when bromine is added to an alkaline solution of pyrogallie acid, it produces a brown color, and as there

* A recent lecture before the Society of Arts, London. From the *Journal of the Society*.

is most bromine removed where there is most silver deposited, the brown coloring matter will be, roughly speaking, proportional in quantity to the density of the negative, unless some of it is removed. There is, perhaps, no *prima facie* reason why an image of this composite character should be objected to. Indeed, the presence of this brown stuff may improve the negative if the film has too little silver in it to give proper density alone, or if the exposure has been too short to change a sufficient amount of the silver bromide into the developable condition, or if the development has been unduly curtailed. It is easy to see, therefore, that a cheap manufacturer and an incompetent, rule-of-thumb photographer may have definite reason for advocating the use of the stain-producing developers. But to rely upon staining matter in the making of negatives is to lean upon a broken reed. The residues obtained by the partial destruction of some complex organic substances are almost pitchy in character, and seem to be very unalterable by ordinary atmospheric influences. But the staining matter produced by the oxidation of developers, so far as I have yet discovered, is never of this kind. Pyrogallie acid generally yields brown products, inclining sometimes to red and sometimes to yellow; but twice I have obtained solutions of so fine a deep blue color that it might have been mistaken for Prussian blue. These blue colors, on standing for a few hours, faded to a yellowishbrown. The deep reddish brown color obtained by simple aerial oxidation of a solution of pyrogallie acid and sodium carbonate becomes perceptibly lighter in a day or two when bottled up, and in a week or so may have lost perhaps half the depth of its color. I think one is quite justified in saying that neither the quantity nor the quality of these staining matters can be controlled, that they are in every way uncertain, and that, therefore, they ought to be rigorously excluded, or perfectly removed, from every negative of value.

And these are far from being all the reasons why the presence of staining matter in negatives should be avoided. A silver image is reliable, and can be chemically worked upon with perfect certainty as may be desired. But staining matter cannot form a foundation for afterwork, and it will suffer change with almost every operation upon the negative. Its color will change and rechange, and by washing it will, under some circumstances, be partly removed. We know very well that when a part of the image is removed by applications to the surface of the film, the shadows lose a greater proportion of density than the lights, because the dark detail is in the upper or outer surface of the film only, and so is more easily attacked. Therefore, granting for the moment that a negative with an image that consists partly of staining matter has correct gradation, if a part of the staining matter is removed the gradation will be falsified, and this alone would be sufficient reason for condemning the use of staining matter in negative making.

There is another source of staining matter, namely, the oxidation of the developer by its exposure to the air during development. The coloring matters so produced may or may not be the same as those resulting from the action of bromine, but, so far as my experiments go, they behave in a similar manner with reference to those changes that are of practical interest to photographers. The darkened solution will soak into the gelatine and color it more or less uniformly, and it appears that it may perhaps also intensify the image by deposition upon it, if we take into account recently published experiments. Mr. A. W. Dolland* has shown how by the use of glycerine gold may be deposited upon the metal in a platinum print, the platinum apparently remaining quite unaffected, and merely determining by "contact action" the precipitation of the gold from a solution that is ready to deposit it upon the least disturbance. Mr. E. J. Wall† has confirmed the results of earlier workers, who found that silver might be similarly deposited. And coming still more closely to the point under discussion, Dr. R. E. Liesegang‡ has recently observed that substances of the nature of pigments may be deposited upon a metallic basis in an analogous manner. He found that the staining matter produced by the aerial oxidation of pyrogallie acid, hydroquinone, and similar substances in alkaline solution would deposit upon and intensify the image of a silver print. A solution of amidol with carbonate of soda he found would deposit colored oxidation products upon the image of a platinum print. It is, therefore, but natural to suppose that probably sometimes the staining matters produced by aerial oxidation in developers will deposit upon the image in negatives, and add to the oxidation products that are already there, produced by the action of the bromine as before described. I have made one experiment in this direction, by soaking part of a negative in an alkaline solution of pyrogallie acid, allowing it to remain until the solution and the negative were both well colored, and then washing for a short time. The color, of course, retarded printing, but I could not discover any intensification effect. It is possible that the staining matter produced by aerial oxidation may attach itself more readily to the image when the image is freshly formed, or it may be that it does not attach itself to the image at all under the conditions which hold during development.

Every photographer knows how to set to work to avoid the production of staining matter, but I think that very few know how to get rid of it when it is in a negative. The usual method is to apply an acid solution—a so-called "clearing solution." The stain may disappear, and then the photographer imagines that it has gone. The error of this empirical and rule-of-thumb method can be easily demonstrated. If hydrochloric acid, sulphuric acid, sulphurous acid, or alum, is added to an oxidized alkaline solution of pyrogallie acid, the brown color is changed to a lighter brown, and immediately a yellowish insoluble matter begins to fall out of solution, and continues to increase in quantity for some considerable time. In a negative where there is not much stain this change of color may cause it to disappear, and the superficial observer would then think that he had got rid of it, while really he had made it, or a large part of it, more per-

manent than before by rendering it insoluble. It is easily shown that this precipitated matter generally constitutes a very important part of the staining material, by dissolving it in carbonate of soda and comparing the color so obtained with that of the original or of the part not precipitated. Citric acid differs from the acids mentioned above, in that it gives no precipitate, but citric acid and alum together give a copious precipitate, even when the quantity added is many times more than sufficient to render the solution strongly acid.

It appears, however, to be possible in aggravated cases to get a small residuum of stain from the use of pyrogallie acid, and rather more from the use of hydroquinone, which it is very difficult indeed, if not impossible, to remove. This residual stain I find to be quite unaffected in appearance by any of the usual clearing solutions, unless they contain iron, and then the color is somewhat changed in tint, and if anything a little darkened. It may be remarked, also, that staining matters vary somewhat, and that exceptions may be found to the results that I have described, but I believe that such exceptions, if any exist, will be found so rarely that it will be practically impossible to take cognizance of them in framing rules for general work. Ferrous oxalate has often been recommended as the most perfect developer when stainless negatives are desired, but although ferrous oxalate is a very useful reagent, I cannot confirm the superiority that is claimed for it. Every developer in use will give clean, grayish black negatives, if properly employed, but by making a careful comparison of ferrous oxalate with eikonogen on a plain gelatine film, I find the iron developer to leave a slight color, which is very difficult, if at all possible, to remove, while the eikonogen leaves none. I have no doubt whatever that metal, amidol and rodinal would all show a like, if not a more marked, superiority. It may be observed that in making such comparisons it is necessary to use a simple gelatine film, because the stain left by ferrous oxalate, when it is applied in the same manner as is usual in development, is easily masked; and it should be understood, too, that the difference is slight. Still what difference there is, is in favor of the alkaline developer.

The rules for practical work that I have deduced from my experiments I have followed for some years with uniform success, nor have I ever heard of dissatisfaction from those who have accepted my suggestions in this matter. I believe that the greatest freedom from stains due to the developer is secured by the use of an alkaline developer with sufficient sulphite, and fixing in a solution of hyposulphite to which sodium sulphite and sodium carbonate have been added. A very few minutes washing between development and fixing is sufficient, but the fixing solution should not be used after it gets dirty or discolored. After thorough fixing should follow a thorough washing, and with a well coated plate this will be a matter of two or three hours or more. By this method any staining matter is kept in its most conspicuous form, and in its soluble and therefore most readily removable condition; and it must surely be allowed that this is the right principle to work upon. Alum should never be used until the washing is finished, because it retards the washing; so-called "clearing solutions" should not be used, both because they tend to make the stain less obvious, and they make its removal impossible; acid fixing baths should be avoided for the same reasons, and if they harden the film, their use is still more detrimental, because in doing so they render the washing more tedious or less perfect.

Having obtained a pure silver image, it may be found that its density is not suitable. It is well that the density should never be too great, because there is no practically useful method of reducing it that does not alter the gradation. On the other hand, intensification is certain and easy, and does not falsify the gradation, when done in a suitable manner. In papers read before the Photographic Society and the Society of Chemical Industry, I have detailed the chemistry of mercurial intensification, and shown that ferrous oxalate is the only reagent that can be relied upon to follow mercuric chloride. Potassium silver cyanide is not suitable, because the image it gives is not of constant composition, and is not permanent; ammonia is unreliable, because it gives images of complex and varying composition, which cannot reasonably be expected to be permanent; all simple alkalies are out of the question; sodium sulphite gives a pure metallic image, but in smaller quantity than the original image, and often, therefore, gives no intensification effect; sodium hyposulphite also gives an image containing a less weight of metal than the original, and, besides, is likely to give very complicated unstable images if used sparingly. Ferrous oxalate, on the other hand, is a perfect reagent, leaving every atom of silver in the original image with an atom of mercury added to it.

The most excellent point of this method of intensification is that, so far as I can discover, there is absolutely no loss of even the faintest detail, but a perfect and proportional action throughout. But this very excellence has proved a drawback in the hands of dirty workers, and workers with unclean plates. A silver stain will be intensified as well as the silver image, and must be so if the action is perfect. I know of no failure by this method not due to imperfect washing or other faulty work. But some photographers say they have found alkaline developers, or alkaline developers without the alkali (if the expression will pass), better than ferrous oxalate, and they have recommended these reagents. I am sorry to say, without a knowledge of their action. If they work as they are stated to do, "cleaner" than ferrous oxalate, that is a pretty sure indication that they are less perfect, unless the only difference is due to the precipitation of the lime in the water when oxalate is used. I have tried many of these solutions, and none of them are reliable. By the use of them, mercury that ought to be in the image is lost, and one cannot tell how much mercury will be so lost, nor from what part of the image it will come. It is hardly conceivable that the mercury lost can come proportionately from every part of the image, and if the loss is not proportional throughout, the density gradation of the negative is upset.

Sodium sulphite, when applied alone, removes both silver and mercury from the bleached image, but with

a developing agent, whether with or without alkali, I have never found any silver in the solution.

Eikonogen alone I found to act very slightly. With sulphite a great deal of mercury was lost. Eikonogen 12 grains, sodium carbonate 25 grains, and sodium sulphite 25 grains, to water 1 ounce, acted well, but 19 per cent. of the mercury was lost. Metol alone gave no perceptible action. Metol 2 grains, sodium sulphite 4 grains, to 1 ounce, acted well, but very much mercury was lost. Metol 4 grains, sulphite and carbonate 24 grains each, to 1 ounce, acted well, but 32 per cent. of the mercury was lost. Amidol 2 grains and sulphite 20 grains to the ounce worked well, and 10 per cent. of mercury was lost. This appeared hopeful, so I tried amidol 8 and sulphite 20, but this was useless, as its effect was very slight indeed within a reasonable time. So I diminished the amidol instead of increasing it, and tried amidol 1 and sulphite 20. This worked well, but 42 per cent. of the mercury was lost. On mixing the amidol and sulphite, sulphurous acid is set free. By adding ammonia to the mixture a blue color appears when the alkali is in a little excess, and by adding ammonia in quantity, just insufficient to produce this color, a solution may be prepared that will remain slightly alkaline throughout the reaction. Such a solution acts very energetically, but a very large quantity of mercury was dissolved by it. Pyrogallie acid 3 grains, sodium sulphite 8 grains, ammonia 3 minims to the ounce, gave a loss of 29 per cent. of the mercury, and the solution was much more colored than in any other case. Pyrogallie acid with sulphite slightly acidified was no better.

In some cases, as stated above, I have estimated the actual proportion of mercury in the solution, and therefore lost from the image, but these numbers must be taken as only giving a general idea of the amount. In some cases, by prolonging the action a little it would have been increased, and probably in no case would the same loss occur by repeating the experiment.

Thus I am obliged to come to the same conclusion now that I did when I first drew attention to the chemistry of mercurial intensification, namely, that ferrous oxalate is the only satisfactory reagent to follow the application of mercuric chloride. I show an example in which this method of intensification has been carried out on various parts of the same negative, once, twice, three times, and four times, without a suggestion of stain or trouble of any sort. It should be noted that this repeated application of the process is a very severe test of its cleanness when properly carried out. If there had been the slightest false deposit of mercury at any stage, this would have been doubled by the next treatment, and increased to four times and to eight times by successive treatments. Silver would have increased similarly, but to a still greater degree. I could show many negatives intensified by this process, but they are similar in appearance to unintensified negatives and therefore would not be instructive.

There is only one other matter that I will refer to at present, and that but briefly, namely, the getting rid of the hyposulphite from the negative. Experience appears to indicate that if a negative is of a satisfactory density, the small amount of hyposulphite left in it after from two to four hours washing does no harm. But if the negative is to be intensified, any hyposulphite will cause a precipitate of mercury salt, and so give a false deposit. This would, as a rule, matter but little, but for the fact that a gelatine negative is always difficult to wash evenly, and such a false deposit will, therefore, almost always occur in patches. If the gelatine film is of exactly the same thickness throughout, equal washing all over is difficult, but in most plates there are variations in the thickness of the film that make it impossible, unless it is so prolonged as to be practically perfect in the thickest parts. What we want is a reagent that will oxidize the small residue of hyposulphite into sulphate, which is quite inert, without affecting the image or attacking the gelatine. I do not know of any reagent that will do this. Peroxide of hydrogen, as described, appears to be excellent, the general idea being that it produces sodium sulphate and sulphuric acid from the remaining hyposulphite, but this is a mistake. It produces no acid, and only about one-third of the sulphur is oxidized to sulphate. By mixing sodium hyposulphite with a large excess of the peroxide, and allowing them to remain together for three days, less than half the sulphur was changed to sulphate, and whatever change had been produced it was of little, if any, use, for the solution still gave a precipitate with mercuric chloride. Peroxide of hydrogen appears, therefore, to be of no avail; but, even if it were, it would be a very unsafe reagent in the hands of ordinary photographers, because its strength is very liable to decline. It may in a few months be only one-tenth of its original strength, and a bottle freshly opened, though originally without doubt of full strength, may be found to contain only a third of the stated quantity; and these changes lead to no alteration in the appearance of the liquid, and can only be recognized by a direct test. These uncertainties render it of very little use in the hands of those who are unable to estimate its strength. Alum and acids decompose sodium hyposulphite, but a mixture of alum and hydrochloric acid acts very slowly upon a weak solution of it, so slowly that one might be tempted to say that it also was useless. I find, however, that a fairly well washed negative is made more fit for intensification by treating it with an acid solution, or an acidified alum solution, and washing again, and I fancy that the improvement is not due merely to the extra washing that it gets. Whatever may be the actual change brought about by this treatment, I find that it is advantageous from a practical point of view, and that it is a desirable precaution to take.

THE BERLINER PATENT.

THE Harrison International Telephone Company recently obtained opinions from several eminent firms of patent lawyers in regard to the validity of the Harrison and Ford telephone patents, all of the opinions declaring that there is no infringement of the Berliner patent. The opinion of Messrs. Witter & Kenyon is particularly interesting on account of its analysis of the status of the Berliner patent, which is as follows:

"The Berliner patent only covers the use of electrodes that are in constant contact and that operate by variations of the pressure of contact. Your tele-

* *Journal of the Photographic Society*, N. S., xviii, 189.

† *Journal of the Photographic Society*, N. S., xviii, 184.

‡ *Photographic Work*, iii, 121.