

## CHEMISTRY FOR THE AMATEUR PHOTOGRAPHER. VI. PRINTING AND TONING\*

A great number of different processes have been used at one time or another for printing negatives. The earliest printing processes depended upon the fact that silver compounds darken in light, and the first printing paper to be used generally was made by soaking a sheet of paper in a solution of table salt and washing this over with a solution of silver nitrate so as to convert the salt into silver chloride. Paper so prepared was known as "salted" paper on which, after exposure to light behind a negative, a print was obtained which could be toned by the deposition of gold from a solution and then fixed with hypo. A better paper was made by using albumen obtained from the white of eggs. After adding salt to it the albumen was spread over the surface of the paper and then sensitized by treatment with a solution of silver nitrate.

After the gelatin process for negatives was discovered gelatin emulsions were applied to printing papers. Gelatin paper was made by emulsifying silver chloride in gelatin with an excess of silver nitrate and then coating it on paper just as films are coated with the sensitive negative emulsion. The typical gelatino-chloride paper of this type is Solio.

To use Solio, the negative is put in a printing frame, and the paper is put with its coated side in contact with the emulsion side of the negative and pressed into contact by closing the back of the printing frame. The frame is then exposed to daylight and the image printed on the paper, which darkens to a brownish red color. From time to time the depth of the printing is observed by opening the back of the frame. The image must be printed to a somewhat darker color than will be required in the finished picture. When printed the paper is removed in a subdued light and the print is toned by immersing in a solution containing gold so that the metallic gold is deposited on the print, giving it a purple color. After toning, the print is fixed in a hypo solution and washed. A toning process is necessary with all printing-out silver papers, such as Solio, albumenized paper, or salted paper, because if the printed-out silver image is fixed without toning, the fixing bath changes it to an ugly yellow color and a very poor-looking print results. The gold toning produces a rich-looking, permanent image which varies in color from brown to purple; these colors, indeed, used to be regarded as the only satisfactory colors for photographs.

The chief use for printing-out papers at the present time is for the making of photographers' proofs. For this purpose the negatives are printed, but the prints are not toned or fixed, and while they are satis-

\* This series of articles is based upon selected chapters from "Elementary Photographic Chemistry" and "The Fundamentals of Photography," published by the Eastman Kodak Company, Rochester, New York. Cuts are by courtesy of the Eastman Kodak Company.

factory for examination, they cannot be kept because they darken in the light, the photographer supplying them only as samples to show the pose and expression, and making permanent prints to order later.

Quite early in the history of photography it was discovered that many substances besides the salts of silver are sensitive to light. One process of printing, the platinum process, is founded upon the sensitiveness to light of iron salts. If paper is coated with ferric oxalate, which is a green, soluble salt of iron, and this is exposed to light, the ferric oxalate is changed into ferrous oxalate, which is insoluble, so that a sheet of paper thus prepared and printed will, after washing, give a faint image consisting of ferrous oxalate. If, to the ferric oxalate with which the paper is prepared, a solution of a platinum compound is added and then, after printing, the faintly visible image is put into a solution of a soluble oxalate, the ferrous oxalate is dissolved and attacks the platinum salt, which is not affected by the ferric oxalate, precipitating metallic platinum on the paper so that an image is obtained consisting of black metallic platinum.

Another process depends upon the fact that gelatin containing bichromate becomes insoluble in water on exposure to light, and this process is known as the "pigment" process or more commonly as the "carbon" process, the name being derived from the fact that the gelatin used in the early days of the process contained finely divided carbon or lamp black to act as a pigment. Such a printing paper is made by coating the paper stock with a thick gelatin solution containing finely divided pigment suspended in it. The pigment is chosen according to the color of the print required. For a black image it may be lamp black, for a red image red ochre or burnt sienna, and for images of other colors any permanent and stable pigment of the color desired which can be finely powdered. After the coated gelatin has been dried the paper is immersed in a solution of ammonium or potassium bichromate or ammonia and again dried. This bichromated gelatin is quite soluble in hot water, but if it is exposed to light it becomes insoluble where the light has acted upon it. The bichromated gelatin is, therefore, printed under the negative in the same way as a Solio print. No visible image is produced, and to get the visible print it is necessary to wash away the soft gelatin. The gelatin, which has been hardened by the action of light, is on the surface of the print and the soft gelatin is at the back, so in order to develop the print it is put face down onto another sheet of paper and placed in hot water. After a short time the soluble gelatin begins to ooze out at the edges of the print and the whole of the original paper can be pulled off, leaving the image covered with a sticky mass of partly dissolved gelatin on the paper to which it has been transferred. This image is then washed in hot water until all the soluble gelatin has been washed away, leaving a clear image of the pigmented gelatin on the paper.

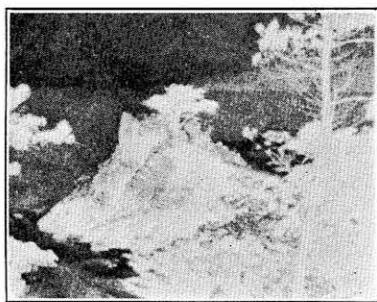
All these printing-out processes require a long exposure to strong daylight, and they have become more or less obsolete owing to the trouble of working them and especially the difficulty of judging the correct exposure with such a variable illuminant as daylight. They have been displaced by printing processes in which the paper used is coated with an emulsion. This paper, known as development paper, is exposed behind the negative and is then developed, in the same way as a negative, to give a visible image.

The oldest of these development papers is bromide paper. This paper is coated with an emulsion very similar to the ordinary negative emulsions but of somewhat less sensitiveness. The paper is very sensitive to light and must be worked by red or orange light only. The exposure for printing is, of course, very short and the paper is, in fact, mostly used for enlarging, the image of the negative being thrown upon the sensitive bromide paper by a projection lantern so as to obtain an enlarged picture from the negative.

About 1894 Velox paper was introduced and was an entire novelty, since, while it is similar to bromide paper in that it is exposed to an artificial light and then developed and fixed, it is so much less sensitive than bromide paper that it can be worked in a room lighted by a weak artificial light and does not require a special darkroom, from which fact it was known as "gaslight" paper. Since the introduction of Velox other "gaslight" papers have been made and at present almost all prints made by contact from negatives are made on papers of this type. Velox is about a thousand times slower than bromide paper so that it can be handled safely in any subdued light. It requires an exposure that ranges from about 2 seconds to about a minute, depending on the density of the negative and the grade of Velox used, at one foot from a 25-watt Mazda lamp, and it is characterized especially by the extreme rapidity and ease of its development, from which its name is derived, developing fully in about 30 seconds. It is consequently possible by using Velox to make prints in comfort and with great rapidity, the old troubles of judging the extent of the printing, and the difficulties with toning baths being entirely absent with this simple and convenient printing medium.

Velox paper is made in grades of contrast to fit different types of negatives. The paper was originally made in one grade only but later it was found necessary to supply other grades suitable for negatives of varying contrasts.

If we make three negatives of the same subject in succession, giving each exactly the same exposure, and then develop these for different lengths of time so that the first will be under-developed, the second correctly developed, and the third over-developed, the first negative will have a short range of contrast, the second a medium range, and the third a long



Soft negative of little contrast

Print from opposite negative on  
No. 4 Velox

Average negative of medium contrast

Print from opposite negative on  
No. 3 Velox

Hard negative of strong contrast

Print from opposite negative on  
No. 2. Velox

FIGURE 1

range. If we then print the first negative on No. 4 Velox, the second on No. 3 Velox, and the third on No. 2 Velox, we shall get almost identical prints on all three papers provided that the contrasts of the negatives just fit the various grades of the paper. This is shown in Figure 1.

We might think that No. 4 Velox would always give a more contrasty print than No. 3 Velox; it will if both papers are printed from the *same* negative, but if the No. 4 Velox is printed from a flat negative and the No. 3 Velox from a normal negative, then the No. 4 Velox will compensate for the flat negative and give a *normal* print, just as the No. 3 Velox gives a *normal* print from a normal negative, and the No. 2 Velox a *normal* print from a contrasty negative. Sometimes a negative of a contrasty subject is over-developed so that it gives too contrasty a print even on No. 2 Velox. For this type of negative the very soft-working No. 1 Velox has been provided.

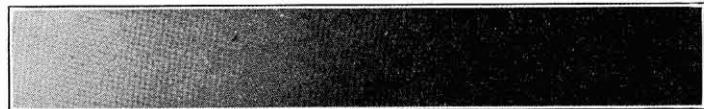


FIGURE 2.—DEGREES OF LIGHT INTENSITIES

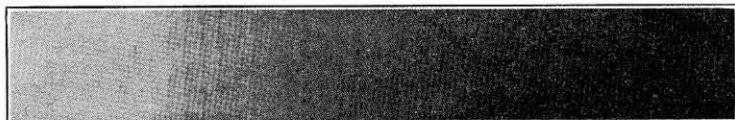


FIGURE 3.—RANGE OF 44 DISTINCT TONES

All the grades of Velox give the same range of reflecting powers in the print provided that they are used with negatives which will enable this range to develop. Suppose we take a black wedge which contains all the degrees of light intensities, from absolute opacity at one end to absolute transparency at the other end and make a print of it. We should get the result shown in Figure 2. This shows the entire range of reflecting power of which the paper is capable, the range varying from white paper at one end to the blackest silver deposit which the paper can give, at the other.

With any "velvet" surface paper, such as Velvet Velox, we shall find that the white paper will reflect about twenty-five times as much light as the deepest silver deposit. The number of distinct tones which are included in this range from white to black depends, of course, on the ability of the eye to distinguish them. The eye can actually see about one hundred distinct tones in such a range.

In Figure 3 is shown a range of tones made up, not as a continuous

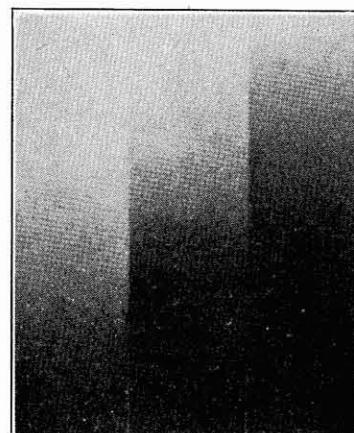
wedge, but of forty-four distinct tones. The number which can be seen in the illustration is less than the number which the eye can distinguish in a print because of the limitations imposed by the process of halftone reproduction. If the full one hundred tones which the eye can distinguish in a print were reproduced by the halftone process the halftone illustration would look like a continuous wedge.

In Figure 4 the same wedge has been printed on all three papers, and it will be seen that No. 4 Velox has reached its full blackness only a short distance up the wedge, No. 3 Velox has gone farther, and No. 2 Velox has gone the farthest of all, so that while all three papers will give the same range of tones, this range is impressed on No. 4 Velox with only a short range of densities in the negative; for No. 3 Velox a longer range is needed, and for No. 2 Velox a still longer range.

The range of densities required in a negative to just print out the full range of tones on a paper is called the "scale" of the paper and this is measured by trying an increasing series of exposures until the range of exposures which will just give the whole range of tones on the paper is found; that is, if an exposure of one second to the bare paper with no negative will just give the first perceptible difference from white paper, so as to show the first trace of tint on the paper, and an exposure of twenty seconds will give the deepest black the paper is capable of rendering, so that no increase of exposure will produce any denser black, then we should call the scale of the printing paper 1 to 20.

Thus the word "scale" applied to a printing paper does not refer at all to the range of tones in the print. It indicates the range of contrast in the negative which should be printed on that paper. A paper with a scale of 1 to 20 will require a negative in which the densest part lets through  $\frac{1}{20}$  of the light transmitted by the clearest part, because if this negative is printed on that paper the print will just have the whole range of tones from white to black completely printed out, each tone in the print corresponding to a density in the negative, there will be no differences of density in the negative unrepresented by differences of tone in the print.

No. 1 Velox has a scale of about 1 to 30 and is used only for very contrasty negatives. No. 2 Velox has a scale of about 1 to 20 and is suitable for printing from contrasty negatives. No. 3 Velox has a scale of about



No. 4                    No. 3                    No. 2  
Velox                    Velox                    Velox

FIGURE 4



FIGURE 5.—PRINT SHOWING EMPTY HIGH LIGHTS

contrasty for the negative; if, for instance, we print a hard negative (one that has strong contrast) on No. 4 Velox, then we shall have to sacrifice a part of the scale of the negative; either we shall get the high lights empty and white, as shown in Figure 5, or we shall get the shadows blocked up, as shown in Figure 6. On the other hand, if the scale of the paper is too long for the negative and we print a soft negative (one that has little contrast) on No. 2 Velox, for instance, when we should have used No. 3 Velox, then we shall get a gray, flat print, as is shown in Figure 7.

With paper, as with film, the density of the picture is controlled by the duration of the exposure and the development, but whereas with films the contrast is dependent upon the time of development, the contrast increasing as the development is continued, with paper the contrast is fixed by the maker, and after a few seconds the development does not change the contrast of the print at all but only affects the density of the deposit.

If a print is over-exposed, it can be taken out of the developer before it is fully developed, and if under-exposed, it can similarly be forced in

1 to 10 and is suitable for printing from negatives of moderate contrast, while the very flattest and least contrasty negatives, which are the result either of excessive over-exposure or under-development should be printed on No. 4 Velox, which has a scale of about 1 to 5.

It is important to choose the grade of paper correctly for the negative. If the paper is too



FIGURE 6.—PRINT SHOWING BLOCKED SHADOWS

development, though there is some risk of yellow stain if development is continued too long. The best results can, of course, only be obtained by getting the exposure right and giving the normal time of development, which is about 30 seconds. The matter of greatest importance for getting really first-class prints, therefore, is to give them the right time of exposure.

Before starting to print a number of negatives they should be classified for contrast so as to choose a suitable grade of paper for printing them; that is to say, put the negatives in envelopes according to the grade of Velox on which they are to be printed. Now take the negatives in each of these envelopes and divide them again into three more classes—normal negatives having average density, thin negatives, and dense negatives. When printing, if we take the exposure for the normal negative as standard, then the thin negatives will require half this standard exposure and the dense negatives will require twice, while sometimes we may possibly meet an exceptional negative—very thin or very dense—which may require one-fourth or four times the standard exposure. Having classified our negatives in this way, in order to get our exposures right we need know only the exposure on each grade of Velox

paper for our standard negatives, and if we print with a 25-watt Mazda lamp at a distance of one foot, we shall find that the exposure for a standard negative will be about 20 seconds for No. 2 Velox, about one minute for No. 3, and one and a half minutes for No. 4. These figures are to be taken only as a guide, and when a new light or a new package of paper is used for the first time, trial exposures should be made with the standard negative, giving, say, 15, 20, and 30 seconds' exposure, so as to select the exposure which develops to the right density with the correct time of development.

It is best always to use the same standard negative for testing a new paper or a new printing lamp and any other new conditions that may arise in printing, as more useful information will be gained by making tests with

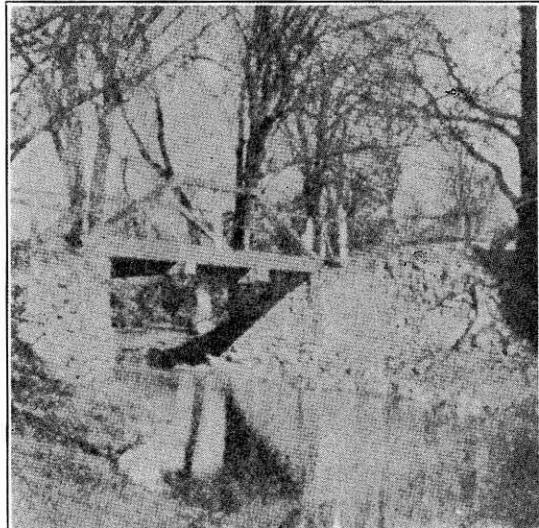


FIGURE 7.—GRAY, FLAT PRINT

one negative only than if a different negative is selected each time a test is to be made.

If the subject of exposure is dealt with in this way, if the negatives are classified for density before printing, and a test is made on a standard negative, it will be found easy to print a large number of negatives on several grades of Velox paper and get a very high percentage of first-class prints with normal development.

With regard to development and after-treatment of the print, there is very little to say, since the matter is fully explained in the instruction sheets furnished by the manufacturers. It is best to buy the ready prepared developers such as Velox Liquid Developer or Nepera Solution and to follow the directions given.



FIGURE 8.—ENLARGEMENT OF PART OF A SNAPSHOT

size; it is a matter of composition and balance, of judgment in the choice of subject and of the moment of exposure, and of finish and quality in the result.

The great value of enlarging is that parts can be chosen from a negative and enlarged to make very pleasing pictures, where the whole negative if printed as a contact print would be by no means satisfactory. The print shown in Figure 8, for instance, is an enlargement of a film negative. This negative was taken at the seashore as a snapshot exposure, the figures being very small and in the corner of the negative so that if the negatives were printed as a whole it would be very unsatisfactory. While a contact

When fixing prints, take care that they do not lie on top of one another in the fixing bath without change so that each print will get its supply of fresh acid hypo.

#### Enlarging

While contact prints are satisfactory to show one's friends, a time comes when we want to attempt something more ambitious and to make photographs which we can hang on our walls or submit for exhibition, and then we feel that we want something more than an ordinary print and something more than an enlarged print; we want to make a picture. The difference between a picture and a print is, of course, not a matter of

print, trimmed as is shown in the enlargement, was not much larger than a postage stamp, an enlargement of the figures in it, however, made a pleasing picture.

Another illustration of what can be done in enlarging is shown in Figure 9, where two negatives have been enlarged together to make a combined picture. The lower half of the original scene, of which the church and trees form the upper half, consisted of a ploughed field, so that the foreground in the original negative was very unsatisfactory. By taking another foreground, however, taking care, of course, that the lighting was the same, and shading the foreground of the first negative so that it did not print in enlarging, then changing the negative in enlarging and substituting the foreground negative, the two have been printed into one another with the result shown. Some photographers are very clever at making these combined enlargements.

The introduction of vertical enlargers, in which the focus is maintained automatically while the degree of enlargement is varied, has made enlarging a very simple operation.

When making enlargements from negatives of varying quality, the enlargement can very often be improved by controlling the exposure, allowing more or less time on different parts of the print.

Practically all negatives, except those that were badly under-exposed, contain much delicate detail that is scarcely noticeable in a small contact print but is clearly seen in an enlargement. The absence of detail in parts of the light or dark tones of a small picture is not displeasing, but in the case of an enlargement these areas, being larger, are much more conspicuous and would be improved if more detail could be obtained. If the negative shows detail in these areas, it can be recorded in the enlargement, and, what is of even greater importance, the contrast between the various tones of the picture can also be increased or decreased as much or as little as desired by locally controlling the exposure when making the enlargement. In order to do this, the light is allowed to act on the whole picture as long as is necessary to print fully the dark tones. Then a piece of cardboard is held in such a position between the lens and the

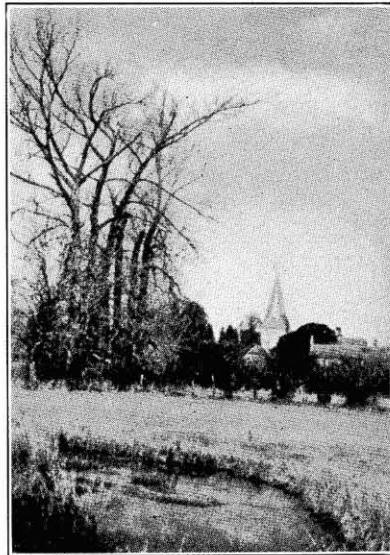


FIGURE 9.—COMBINED ENLARGEMENT FROM TWO NEGATIVES

paper that it prevents the light from reaching and consequently overprinting the part of the picture that has been fully recorded without preventing it reaching the parts that are not yet fully printed.

### Toning

In the earlier printing processes used by photographers—those in which the image was obtained by the continued action of light and which were toned by the deposition of gold from a toning bath—the prints obtained were in various shades of purple and brown, and these shades became so associated with photographs in the mind of the public that when the black and white prints made on Velox and bromide papers began to displace the earlier Solio and Aristotype prints, the general public would scarcely recognize them as "photographs" at all, and a demand soon arose for some method of toning the black images of bromide and Velox prints to a brown or sepia similar to that of the gold-toned printing-out papers.

It seems to be characteristic of mankind to want what they have not got, and it is interesting to note that with the earlier printing-out processes which easily gave warm tones, chemists were anxiously working to get methods of obtaining black and white prints, while with the developing-out processes, which naturally give good black and white prints, photographers desire to obtain warm sepia and brown tones.

The processes for obtaining sepia prints from the black developed-out images all depend on one chemical reaction; namely, that by which silver bromide is converted into silver sulfide. Silver sulfide is a dark colored, almost black, substance well known to the housekeeper—if not by name—as the tarnish which appears on silverware after it has been some time in the air, the surface of metallic silver being attacked by sulfur compounds in the air, which generally come from the products of combustion of gas in the cooking range or from coal heating devices.

Now, when any chemical substance *can* be produced by the interaction of two other chemical substances in solution the question as to whether it *will* be produced depends upon whether it is more or less soluble than the substances which can form it. Silver sulfide is less soluble than silver bromide so that when silver bromide is treated with a solution containing sulfur in a free form it is changed into silver sulfide and the silver sulfide is deposited in its place. On the other hand, metallic silver, such as that which forms the image in a developed print, is less soluble than silver sulfide and consequently we cannot change it into silver sulfide by simply treating it with a solution containing free sulfur, but if in this solution we have some substance which will dissolve metallic silver, then we can change the metallic silver itself into silver sulfide. It is on these principles that the sulfur-toning processes are based.

One toning process depends upon changing the silver image of the print back into silver bromide. Now, we know that silver is obtained from silver bromide by reduction, just as iron is obtained from iron ore, and therefore we can get back silver bromide from silver by oxidation, which is the reverse process to reduction. If we use any solution which will oxidize silver and have potassium bromide present in the solution, the silver image will be turned into silver bromide.

The usual way to do this is to treat the black print after fixing and washing with a solution containing potassium ferricyanide, which is an oxidizing agent, and potassium bromide and this turns the black silver image into a yellowish white image of silver bromide which is scarcely visible, so that the process is called "bleaching" since the black silver turns into white silver bromide, and then after washing, this silver bromide is treated with a solution of sodium sulfide, which turns it into the brown silver sulfide which gives us our sepia-toned print. So, to make a sepia Velox print by this method, we treated it with the "bleaching solution" which turns the silver into silver bromide, and then "redevelop" this, as it is called, in a solution of sulfide, which converts the silver bromide into silver sulfide and gives us our sepia print.

There is another method of obtaining sulfide-toned prints which is somewhat simpler. We have seen that we cannot turn silver directly into silver sulfide by a solution containing free sulfur unless we have a solvent of silver present in the solution. Now, it so happens that hypo is to some extent a solvent of silver, and also that with a weak acid, hypo gives free sulfur. Alum behaves chemically like a weak acid and it also has the valuable property of hardening the print, so if we put the print which we wish to tone into a solution containing hypo and alum, the silver will slowly be changed into silver sulfide and the print will be toned brown. This change goes on very slowly at ordinary temperatures, but by heating the solution it goes much more rapidly, so that if we heat a bromide or Velox print in a solution containing hypo and alum, we shall get a good sepia tone at the end of ten or twenty minutes without any further difficulty, the only objection being that the bath, like all baths containing free sulfur, and like the sodium sulfide used for redeveloping in the other toning process, smells rather unpleasantly.

Equally good results in sepia toning cannot be obtained with all papers, but a great deal depends on the development of the print. To get good sepias, development should be full; an under-developed print will always give weak, yellowish tones when compared with one in which development has been carried out thoroughly, which will give a strong, pure sepia. It is important to remember this, as two prints which may look alike as black and white prints will tone differently if they have not been developed to the same extent.