CHAPTER II

BLEACHING AND TANNING

After having produced a bromide print of the restricted tonal range demanded by the process, and in the manner described in the last chapter, the next operation is to tan the gelatine matrix in proportion to the silver deposit already present, and to get rid of the silver deposit itself, as thereafter superfluous. Thus, there are three separate operations involved:

(1) Bleaching the silver image in order to convert it into such a form that it reacts with the tanning solution to produce the desired differential tanning of the gelatine.
(2) The actual tanning operation.
(3) Fixing out the silver image when it has served its purpose of regulating the amount of tanning at any given spot.

It is quite common practice to combine operations (1) and (2) in the same bath, but, for reasons which will be discussed later, it is not theoretically sound to do so. The normal bleaching substances employed are salts of copper, in the presence of an excess of an alkali chloride or bromide, so that in effect there is present the chloride or bromide of copper. The tanning agent employed is always a chromium compound, usually potassium bichromate, or sometimes chromic acid itself. The exact mechanism of the insolubilisation of gelatine and other colloids by the chromium salts is not well understood, and in any case need not be discussed in the present instance.

There are slight variations in the results produced by different bleaching and tanning mixtures, and it is advisable for the beginner to adopt one bath and adhere to it until he has the process well in his grip. From the experienced

worker's point of view, however, the variations in results are of so minor a character that almost all formulæ may be taken as of equal value within certain limitations as follows:

(1) The concentration of bichromate or of chromic acid must be approximately equal.

(2) The acid concentration, if any, must be kept low. Bleaching and tanning baths with high concentrations of acid induce higher degrees of swelling in the subsequent soaking, and baths of this type were more common in the early days of the process when contrasting black-and-white prints were advocated, and acid wash waters were often used.

Bleaching and Tanning Bath Formulæ.

(1) SEPARATE BATH METHOD:

It was mentioned above that this method is to be regarded as the only theoretically sound one. The reasons for this statement are several in number. Firstly, we have already laid down a rule that solutions should, as far as possible, be used once only. Now, the ordinary combined bleaching and tanning bath is comparatively costly to compound, and it would prove irksome to many amateurs to renew this after each print. By using the separate baths the copper bleaching solution may be employed repeatedly without contaminating the tanning bath with its decomposition products, and, furthermore, gives visible evidence of its loss of strength by slowing the bleaching, which in itself produces no ill effects. The important bath, i.e. the tanning solution, can be used once only and can then be thrown away, as the cost is not excessive.

Secondly, there will always be differences in density of the bromide print, and even different development factors influence the time of bleaching. In general, therefore, the period required for bleaching will vary from print to print. If tanning is to proceed in the same solution, the time of tanning will also vary from print to print with consequent variation in the necessary swelling conditions prior to

inking. It is, therefore, advised that the small extra trouble of using two solutions be taken, and that the tanning solution be used once only.

The details of the solutions and the method are as follows:

Bleaching Solution:

Copper sulphate 10% solution .	95 parts
Potassium bromide 10% solution .	5 parts

Tanning Solution:

Potassium bichromate 1% solution	10 parts
Potassium bromide 10% solution .	20 parts
Water to	100 parts

Bleach the print in the first bath until only a faint yellowish deposit remains, and allow to remain in the bleacher for 30 seconds after disappearance of the last vestige of black image. Remove and allow to drain. Then immerse, *without rinsing*, in the tanning bath, and keep moving gently in this for 4 minutes. The baths are to be used at temperatures approximating to 65°–70° F. After tanning, wash the print well in running water or in several changes, and just prior to fixing it is a good idea to swab the surface gently with a small wad of cotton wool.

This double-bath method of working is due to some valuable investigations by Venn (*B.J. of Photography*, 1926, vol. 73, p. 358). The beginner, and frequently the more experienced bromoiler, too, is at a loss to account for the peculiar working of some prints, and in these cases it is a great advantage to be able to rule out the bleacher as a source of trouble. With ordinary single solution bleachers, it is often recommended to renew the vitality of the solution from time to time by addition of fresh bath, but in general, a time will eventually come when prints begin to behave abnormally in inking, and on many such occasions the substitution of entirely new bleaching solution cures the trouble in subsequent batches, thus indicating that the limit has been overstepped. Such a state of affairs is impossible with the procedure indicated above.

(2) SINGLE SOLUTION BLEACHER (Crowther's formula):

Copper sulphate 10% solution .	170 minims.
Potassium bromide 10% solution .	130 minims.
Chromic acid 1% solution . .	45 minims.
Water to	3½ ozs.

(3) SINGLE SOLUTION BLEACHER (Acid Type):

	Metric	*English*
Copper sulphate .	80 g.	2 ozs.
Potassium bromide .	80 g.	2 ozs.
Potassium bichromate	4·2 g.	50 gr.
Sulphuric acid .	3·3 g.	40 minims.
Water . . .	1 litre	25 ozs.

For use, dilute one part of this stock solution with five parts of water. In this, as in all single solution bleacher formulæ, it is preferable to employ distilled water, as the lime salts in ordinary tap water have a precipitating effect on the vital reagents. This bleacher contains an excess of sulphuric acid, and will be found to deal successfully with prints of a greater depth of deposit than some of the neutral formulæ.

(4) DR. E. MEYER'S BLEACHER:

This bleacher is simple in composition and efficient in action.

Copper sulphate 20% solution . .	3 parts
Potassium bromide 20% solution .	3 parts
Potassium bichromate 10% solution.	1 part
Water	15 parts
Hydrochloric acid	0·04 part

If the parts are taken as fluid ounces, the hydrochloric acid comes out at 20 minims or drops.

(5) C. J. SYMES' FORMULA:

The following formula is put forward in the latest paper by this well-known worker (*Am. Phot.*, 1929, p. 528).

10% solution copper sulphate . .	5 oz.
10% solution potassium bromide .	5 oz.
1% solution potassium bichromate .	2¼ oz.
Acetic acid (glacial) . . .	8 minims.

For use, dilute one part of the above solution with two parts of water. The bath is preferably made with distilled water, and bleaching is allowed to continue thirty seconds after disappearance of the image.

(6) A Formula not Involving Potassium Bromide:

It will be noted that in all the previously given variants, potassium bromide is universally used as the alkali halide constituent. Some writers recommend that this comparatively expensive salt can be replaced by sodium chloride (rock salt) without detrimental results. The writer has never actually compared two formulæ differing only in that the chemical equivalent of sodium chloride is substituted for the potassium bromide, but the following mixture is entirely satisfactory in his experience.

	Metric	*English*
Copper sulphate	4 g.	1 dr. 20 gr.
Salt (preferably pure sodium chloride)	27 g.	1 oz. 1 dr.
Potassium bichromate	1 g.	1 scruple
Water	480 ccs.	20 ozs.

A few drops of hydrochloric acid are added in order just to dissolve any precipitate which may form. With distilled water, or very soft water where only a small quantity of reagents is precipitated, the addition of acid is unnecessary. The salt is present here in very large excess, but the formula works well in practice. Table salt should not be used for compounding this or similar formulæ, because it normally contains magnesium and calcium compounds which are undesirable in the bleacher. A good grade of rock salt is satisfactory, or pure sodium chloride is not dear.

To those with an experimental bent, the results of substituting salt for potassium bromide in other formulæ would be interesting. The author has made experiments with the double bath tanning solution and finds that the use of the chemical equivalent of sodium chloride in place of the bromide leads to no deleterious consequences. He has, however, not made direct comparisons to detect any slight differences in working which may result.

For the information of those wishing to experiment, it may be stated that 58·5 parts of sodium chloride are chemically equivalent to 119 parts of potassium bromide.

Copper chloride may also be employed in place of copper sulphate, and appears in some formulæ, but there appears to be no particular advantage in so doing, while at the same time the chloride is not so convenient to handle, and is, moreover, more expensive.

It has been stated already that it is preferable to use distilled water for making up bleaching and tanning solutions, and this is especially true if they are to be kept any length of time. In this latter case, those formulæ, which are made up from stock solutions containing one reagent only, are very much preferable. Thus, copper sulphate, potassium bichromate, and potassium bromide keep indefinitely in their respective solutions. If concentrated solutions containing more than one ingredient are made up, and allowed to stand, complicated chemical changes occur which gradually lead to considerable reduction in the efficiency of the bath. The whole question is thoroughly discussed by Venn (*British Journal of Photography*, 1926, Vol. 73, p. 384 *et seq.*).

Fixing and Washing. Whatever method be employed to produce the bleached and tanned image, there remain one or two steps before the print is ready for the bromoil operations proper, i.e. swelling and pigmenting. In the first place it is necessary to get rid of the silver halide which has resulted from bleaching the original silver image. Before, however, this can be done by the simple process of carrying out another fixing operation, it is necessary to ensure that all soluble constituents of the tanning bath shall be eliminated. To this end the print, as it comes from the bleaching bath, must be washed thoroughly. Generally it is better to overdo than underdo this operation. By some a matter of a few minutes in running water or one or two changes is suggested as adequate, but it is far sounder to wash for one hour in running water or in ten or twelve changes so that elimination of copper and chromium compounds is complete. Interaction of these salts and hypo produces a general tanning of the gelatine

irrespective of the original silver deposit. Thus incomplete washing will certainly lead to a possibly slight general tanning, and probably to a much more serious uneven tanning due to more copper and chromium compounds being retained in one part of the image than in another.

After an adequate washing the print is again immersed in 10% hypo solution for two or three minutes, and is finally washed free of the bulk of the hypo by means of, say, twenty minutes in running water, or half a dozen changes. Thereafter the print may be proceeded with at once, or, preferably, may be dried first.

Direct Inking or Preliminary Drying. In general it may be taken that for those not yet expert in the process, preliminary drying is always to be recommended. When the print is dry it is easy to standardize the exact soaking procedure prior to inking, and a constant degree of swelling is not difficult to attain. When the print has come from the final washing water after bleaching and fixing, it may contain a very indefinite amount of water, and frequently the gelatine, in the course of many operations, has reached a rather sensitive condition. This condition may present its own advantages, and C. J. Symes recommends that the best bromoil transfers are to be made from prints not first dried prior to pigmenting. Presumably the easy differentiation of tones in the deeper shadows is not reproducible when the matrix has dried and contracted. As will be learnt during our discussion of the peculiarities of transfer, the behaviour of the shadows is the crucial factor, and it is worth experimenting with any procedure which facilitates the transfer of these deep tones. Generally, however, those making their début in the process will not be concerned with transfer, and it is good advice in this case, always to dry before swelling prior to pigmenting.

Abnormal Temperature Conditions. Most sets of directions for working in bromoil assume that solutions, washing waters, etc., are all at a mean temperature about 65° F. This ideal mean temperature, like the chemist's "ideal gas," is not so frequently met with in practice. It is necessary to devote a few words to a consideration of what

effects are produced by variations from the mean temperature, and what precautions are advisable to counteract such variations.

It appears from the experimental work which has been carried out that one factor of prime importance is that there should be no sudden variations in temperature during the bleaching, tanning, fixing and washing operations discussed above. Constancy of temperature is of more importance than the actual temperature. Work can be successfully carried out down to 40° F. if necessary, although these low limits are better avoided wherever possible. As far as developing operations at low temperatures are concerned amidol is the only satisfactory developer, and even that works much more slowly. Venn deals with this matter at another point in his interesting paper before referred to (*British Journal of Photography*, 1926, Vol. 73, p. 401). It appears that a reduction in development factor at low temperatures produces more easily inked prints. As an example, a factor of 8 with a development formula similar to that given here as standard, produced excellent prints at 45° F. A maximum development time of four minutes seems to mark the limit at which prints still ink up readily, and as the development slows up more and more at lower temperatures, this will correspond to an increasingly lower factor the lower the development temperature. The original paper should be consulted for full details, but it will suffice for our practical purpose if we remember that *the development factor should be reduced at low temperatures to an extent corresponding to a maximum development time of four minutes.*

Bleaching and tanning with cold solutions, of course, takes a longer time than normal, but otherwise there appears to be little disadvantage. If the bleaching and tanning solutions are to be warmed for use, the fixing bath should be warmed to the same temperature, and at any rate the first few washing waters should be warmed. If it is inconvenient to carry out the entire washing with water warmed to the same temperature as the other solutions, the first few changes may be so warmed, and subsequent baths gradually reduced in temperature until the temperature of the main supply is reached. Venn

prefers to work throughout at the temperature of the main supply, but this is a Spartan doctrine, and in actual practice no harm appears to result from the above procedure. What often does produce bad results is the sudden plunging from a normal room temperature to the icy cold of main water supply in mid-winter.

Hot weather troubles usually involve nothing more serious than a slight over-swelling of the matrix, which can, in most cases, be corrected by softening the ink. This will be discussed at length in a later chapter.

The "Short" Process. Before closing this chapter it remains to consider an abbreviated method of working which, although discountenanced by some authorities is, from the author's experience, quite reliable, subject to care in observing some small details, and which presents great advantages in some particular cases. It will be noticed in the above description of the normal working of the process that two fixing operations occur, one directly after development, and the other after bleaching and tanning. Provided the print is not exposed to actinic light, the first fixing may be omitted, and the print bleached, tanned and fixed directly after development. A non-staining developer, preferably amidol, must be used, and excess developer must be eliminated by a ten minutes, wash, or several changes of water. This must, of course, be carried out in the dark room, and consequently will not always be convenient or possible. At the conclusion of this short wash the print is bleached, tanned, fixed, and washed in the usual manner as described above. The final washing need be only short, as any residual hypo cannot do any great harm. Dr. E. Meyer is altogether against this method of working, but on the other hand A. C. Banfield recommends it, and from the author's practice there would appear to be nothing against it.

One item must, however, be very carefully watched: the depth of image in the bromide print. It is well known that the apparent depth of a print alters considerably on fixing. In this case, as the print will not be fixed until after bleaching, the final depth must be judged in the developer. This means that allowance must be made for

the gain in depth in the fixing bath. A bright yellow light should be used to judge the depth of the prints, and it is a good idea to have a small bath of hypo handy and actually to fix the trial strips in the ordinary way. The saving in time if this method be employed is very considerable, and, provided the judgment of depth in the developer is correct, the results are excellent.

Summary of Points from Chapter II

(1) Bleaching and tanning formulæ all give similar results. Choose a good formula and adhere to it.
(2) The double bath bleaching and tanning procedure is scientifically sound, and allows economical rejection of once used tanning mixture.
(3) Between tanning and final fixing give a thorough wash—the final wash may be curtailed.
(4) Endeavour to keep bleaching baths, wash waters, fixing baths, etc., at similar temperatures. If temperatures are low, reduce the development factor to give a total development time of 4 minutes.
(5) In the "short" process bleaching follows development without first fixing. Accurate judgment of print depth in the developer is essential.