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SULPHOCYANIDES IN TONING AND FIXING.

SINCE publishing some recent remarks on the use of sulphocyanides in toning, we have been asked by several correspondents if we retained our faith in these salts as fixing agents for silver prints. We are reluctantly constrained to say that we do not. When the subject of a new fixing agent was first introduced to the photographic public four or five years ago, with the promise of a release from the troubles which attended the use of hyposulphite of soda, we addressed ourselves with considerable care to an experimental examination of the matter, and obtained results which gave us considerable confidence in the possibility of superseding hyposulphite by an agent free from the risks to the prints which its use engendered. The experience and observation of the years which have since elapsed have compelled us to modify very considerably the hopes then raised.

The especial points of superiority claimed for sulphocyanides over hyposulphites were stability and freedom from the risk of the decomposition in which sulphide of silver was formed, either in the bath or in the prints; and the capacity of perfectly dissolving the albuminate of silver, and thus removing all traces of a silver salt from the whites of the albuminized print. The first claim can be substantiated, the second cannot. We have not found in any of our experiments, extending over four years, any tendency to deterioration in the prints from the liberation of sulphur, or from any decomposition analogous to that common in the hyposulphites. As regards the presence of silver in the whites, we have never found any advantage in the operation of the sulphocyanides; in this respect the result has not been different to that produced by the use of hyposulphite of soda. The objections to its use arise, however, from another source: we refer to the difficulty of removing all trace of the sulphocyanide of silver from the print. To make the matter quite clear to those who have not given attention to the subject, it may be desirable briefly to restate the reactions which take place in employing a sulphocyanide for fixing purposes. On immersing an unfixed silver print in a solution of sulphocyanide of ammonium, a double decomposition ensues, in which sulphocyanide of silver and chloride of ammonium are formed. If the solution be originally of sufficient strength, sulphocyanide of silver, instead of being precipitated, is dissolved by the excess of sulphocyanide of ammonium, forming a double cyanide of ammonium and silver. Neither this double salt nor sulphocyanide of silver is soluble in water, but perfectly so in a strong solution of sulphocyanide of ammonium. The print, after it has been submitted to the fixing operation, is of course saturated with the solution of double sulphocyanide of silver and ammonium; on removing it to the washing water, this double salt is decomposed into sulphocyanide of ammonium, which, being soluble, passes into the water, and into sulphocyanide of silver, which, being insoluble, remains in and on the print. Here is the difficulty. It is important to get rid of this silver salt, but it is not easy to effect. The plan proposed originally was, after rinsing the print, again to pass it into a fresh bath of sulphocyanide of ammonium, which re-dissolved the precipitated silver salt, and left a mere infinitesimal trace to be precipitated on again restoring the print to the washing water; and this was, to a considerable extent, effective; but the trouble of uncertainty remained. It was difficult to ascertain when the traces of sulphocyanide of silver were removed sufficiently for practical fixing purposes. We have before us now some prints which we fixed with sulphocyanide of ammonium upwards of four years ago, which are as perfect in colour as on the day they were first produced; but we have, on the other hand, some fixed at the same time—probably in a bath which had been used a few times—which have become dingy and discoloured by the action of light. Sulphocyanide of silver is not readily darkened by light, but is affected in course of time; and prints in which traces of it remain gradually lose the purity of the whites, and assume a greyish tint; and the difficulty is to ascertain at what stage the second fixing bath leaves the print with sufficient of the silver salt to risk gradual darkening of the lights. Hence, with all the undoubted advantages of the sulphocyanides as fixing agents, the element of uncertainty remains, and we cannot with confidence employ them.

In the operation of toning they possess, for some purposes, undoubted advantages. Following the formula given at the time to which we refer, in 1863, by M. Meynier, the introducer of the sulphocyanides, we obtained some very excellent results. The formula recommended by that gentleman consisted of six grains of sulphocyanide of ammonium to one grain of chloride of gold in three ounces of water. In our recent experiments we have found that a much larger proportion of the sulphocyanide is better and more satisfactory in its operation.

The toning bath in which sulphocyanide is present has several distinct characteristics in which it differs from the ordinary alkaline or neutral gold toning baths, and some of which are very useful. It appears to give considerable immunity from mealiness; in fact, we have in no case seen mealiness where it has been employed. The tones produced are different; indeed, the pleasant warm tone yielded by the acetate toning bath is in no case obtained by the sulphocyanide bath; but a peculiar range of tones is obtained which, for some purposes, is very pleasing. Three distinct effects may be produced by the use of this toning bath: cold or grey half-tones with brown shadows and darks; rosy half-tones with intense pure blacks; and a uniform tint of a rich rosy purple inclining to a ruby tint.

The first effect of immersing the print in the toning bath