NOTES FROM THE RESEARCH LABORATORY,
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THE EFFECT OF THE IRON CONTENT OF AMMONIUM PERSULPHATE ON ITS PHOTOGRAPHIC REDUCING POWER.¹

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It is well known that different commercial preparations of ammonium persulphate show wide variations in their behavior in attacking the density of photographic negatives. The typical peculiarity of persulphate, namely, its selective action on the higher densities, has received many explanations. In this direction the most important contributions to the chemical mechanism of persulphate reduction are the following:

H. Marshall (*Trans. Edin. Phot. Soc.*, 1900, **23**, 168) showed that the action of persulphate on metallic silver is what is termed auto-catalytic, *i.e.*, it is accelerated by the reaction-product, the dissolved silver sulphate. A chemical explanation of this is the formation of an intermediate *silver persulphate*, which is a stronger oxidizer than the ammonium or potassium persulphate; the action in question may be considered to take place in stages represented by the following chemical equations:

This reaction, the formation of silver ions by the direct attack of persulphate on metallic silver, is very slow.

This reaction, a purely ionic interchange, is very rapid.

Finally, the attack of silver persulphate upon metallic silver, is also a rapid reaction.

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In the absence of silver ions (or other catalyst) the reaction is slow at first, then becomes rapidly accelerated.

By adding silver ions, *e.g.*, silver nitrate or, better, silver sulphate, to a sluggish persulphate solution, the initial retardation is overcome.

It was suggested that this auto-catalytic action of the dissolved silver afforded an explanation of the superproportional action. This, however, is not the case. Unless other factors intervene, the rate of reaction would still be proportional to the density, so that the undoubted acceleration by dissolved silver is not a complete explanation.

Different observers had noted that the water used in making up a persulphate solution affected the action. This was taken up by E. Stenger and H. Heller (*Zeit. Wissent. Phot.*, 9, 73, 1910). They found that, depending upon the amount of chlorides in tap-water, the type of reduction changes from the superproportional to the subtractive. They attribute this 'chloride poisoning' to the formation of relatively insoluble silver chloride, which lowers the concentration of the catalytic silver ions and protects the silver grain from further attack.

It can, however, be shown that even with distilled water free from chlorides the anomaly persists. Schuller (*Phot. Rundsch.*, 1912, p. 236) brought forward more definitely a suggestion often tentatively advanced, namely, differential diffusion. Schuller adopts the silver persulphate or catalytic theory, but considers that superproportional action on the higher densities is much less determined by poisoning in the lower densities than by a restriction on diffusion in the higher densities.

As against these explanations, Lüppo-Cramer (*Colloid Chem. und Photographie*) advanced a colloid chemical theory. He considers that the composition of the developed and fixed negative image is not pure metallic silver, but remains an adsorption compound of silver and photohalide. The amount of photohalide and, *a fortiori*, of normal silver halide, is very small, but it is supposed to be greater in proportion as the exposure is less. There is then more photohalide in the lower densities than the higher. This he suggests is due to a more energetic attack of the developer on the grains of the higher, more exposed densities.

Lüppo-Cramer regards this as an explanation of the peculiarities of photographic reducers. Reducers with a silver halide

solvent present in solution with the oxidizing agents—as in Farmer's reducer—will attack the lower densities more strongly than the upper, and we get subtractive action. On the other hand, in reducers like persulphate, or in chromic acid poisoned with soluble chloride, the lower densities having more halide are better protected from attack.

It is to be noted that the facts and explanations brought forward still fail to account for certain minor characteristics of persulphate reducers. One of these is the already mentioned variation, particularly of initial activity, between different preparations having the same persulphate content. Another is the action of acid and alkali on this initial activity.

Lüppo-Cramer, in support of his photohalide theory, instanced the equalizing action of sulphocyanide (a silver halide solvent) upon ammonium persulphate. This combination was first recommended by Bayley and Puddy (*Phot. News*, 1900, p. 174) as giving a proportionate action.

In the course of some experience intended to test Lüppo-Cramer's views on the negative image, Bayley and Puddy's combination was tried. It cannot be said that it is very satisfactory either chemically or photographically. In the first place, like other complex cyanides, sulphocyanide is attacked by persulphate with the liberation of hydrocyanic acid. In the second, measurements with sensitometer strips show that there is no certainty of proportionate action.

In trying the combination with different persulphate preparations it was observed that they all reacted, more or less vigorously, for *iron*. Further, it was noted that the preparation showing the least initial activity, or the greatest initial sluggishness, gave the weakest reaction for iron, while the most vigorous preparation, one, in fact, very difficult to control, gave the strongest reaction.

The preparations were therefore analyzed for iron, with the results given later.

On adding ferric sulphate to the solution weakest in iron till it was approximately equal in this respect to the strongest, the initial activities were made practically equal. Quantities of iron in excess of this relatively small amount gave reducers of uncontrollable character, the action becoming very irregular and localized.

The small variable amount of iron salt present as an impurity in ammonium persulphate is thus the cause of its variability, and iron, however introduced, is a powerful catalyzer of the action of persulphate on metallic silver. The chemical reactions involved show that we have here a case where a side-reaction supplies more rapidly the auto-catalyst for the main reaction, while the main reagent re-energizes the side reagent or catalyst. Iron, as a ferric salt, *e.g.*, *ferric sulphate*, rapidly attacks metallic silver, forming silver sulphate and ferrous sulphate:

and the *ferrous sulphate* is rapidly reoxidized to *ferric* by persulphate.

so that the concentration of ferric iron tends to be kept up to the initial level. Further, the silver salt (or silver ions) supplied by reaction (4) give the necessary acceleration to the persulphate reaction proper, these reactions being those already noted in equations 1, 2 and 3.

The function of the iron then is somewhat like that of a pilot flame. By immediately furnishing silver ions, through reaction (4), it abbreviates the initial retardation and gets the rapid following reactions in full swing without delay. At the same time, the catalytic action of iron explains in part the effect of acidity and alkalinity on the persulphate reducer. So long as an acid reaction obtains, the iron will be in the active ionized condition. If the reaction becomes alkaline, the iron will be progressively removed by hydrolysis, being converted to ferric hydroxide, which, moreover, is strongly absorbed by gelatine, with a tanning effect and probable reduction in diffusion velocity.

It is necessary to note at this point that this iron catalysis does not stand in any contradiction to the other aspects of persulphate reduction. In particular, experiments with iron catalyzed persulphate strongly support the theory that it is a superposition of diffusion conditions upon auto-catalysis which leads to the characteristic persulphate effect. This superposition of diffusion or coupling of diffusion with a chemical reaction in the photographic layer has been frequently noticed, and we can generalize the present result as follows:

1. If in a photographic process the reaction products affect

(accelerate or retard) the primary action, then the speed of this will depend upon their rate of removal and momentary concentration.

2. These products, if soluble, will tend to diffuse away most rapidly in the direction of regions of lower concentration.

3. From the known structure and distribution of the negative image, diffusion, and hence exhaustion, of reaction products will occur more easily in the lower densities than in the higher. Conversely, there will tend to be a superproportional accumulation of the reaction product in the more strongly exposed regions, the lower layers next to the support eventually acting as reservoirs.

Amounts of Iron.—The percentage quantity of iron involved is not of a very large order, as will be seen by the following data :

Sample	Make	Persulphate	Iron per gram Persulphate	Remarks
No. 1....	Commercial	98.3 per cent.	.0006 gram	Could just be used in in 5 per cent. solution. Quite active at once.
No. 2....	Commercial same firm different stock.	97.8 per cent.	.00162 gram	Could not be used in stronger than 2 per cent solution. Very active at once.
No. 3....	Laboratory product.	98.2 per cent.	.000088 gram	Very inactive; in 5 per cent. solution hardly any action in 15 mins. Iron, alum, or silver nitrate brought it up to No. 2.

In a later communication data on the relation of the iron concentration to the action measured sensitometrically will be given. Meanwhile it may be noted that in a 5 per cent. solution persulphate the amount of iron required to perceptibly affect the initial activity in dissolving silver is of the order of 1 part in 1,000,000.

The tolerance or upper limit of iron permissible appears to be of the order of that found in preparation (2), 1 to 2 parts per 1000 of solid persulphate.

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