

A STUDY OF THE EFFECT OF METALS IN CONTACT WITH SOLUTIONS OF SILVER HALIDES IN VARIOUS SOLVENTS

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During the performance of an experiment by a class of students large quantities of a very dilute solution of silver salts were produced, from which, both for economic reasons and for its effect on the student, it was desired to recover the silver. It occurred to one of the authors that the easiest and most direct way to recover the silver was to convert it into chloride, dissolve this in some solvent like ammonia, and precipitate the silver by treatment with some metal like iron or zinc. Whether metals would precipitate silver from such solutions was not known and a search through the available literature did not indicate that the experiment had ever been tried.

When silver chloride is dissolved in ammonia it is believed that a complex positive ion results which contains both silver and ammonia, $\text{Ag}(\text{NH}_3)_2$. Since more than the equivalent amount of ammonia is necessary to produce solution it is probable that this positive ion is in equilibrium with the silver ion, the concentration of the latter ion decreasing with the increase in concentration of free ammonia. In any such solution, however, there might be enough silver ions so that in contact with metals whose solution tension was greater than that of silver ions the latter might be discharged and the silver deposited. A preliminary trial with such a solution gave a gray powder appearing somewhat metallic.

The solutions of silver salts, left over from the students' experiment, were collected and the silver precipitated by an excess of hydrochloric acid. After washing the silver chloride it was dissolved in rather concentrated ammonia, making a nearly saturated solution. To this was added granulated zinc. Almost immediately the gray deposit formed, together with some gas, probably hydrogen, and towards the end of the experiment

there were formed beautiful silver-white metallic crystals. Much of the gray powder was rather soft and malleable and when rubbed gave a metallic luster. Always there was a larger or smaller amount insoluble in dilute nitric acid, and this appeared to be silver chloride which had been affected by light. After some hours only the smallest traces of silver chloride remained in the solution.

These results were so encouraging that it was felt to be worth while to study the effect of various metals on solutions of the halides of silver, not only in ammonia solutions but in other solvents, especially in the "hypo" of the photographer. It is known that large quantities of the spent "hypo" liquors are discarded without the recovery of the silver contained in them, thus involving a great economic loss of silver as well as of "hypo". While a method is in use for the recovery of the silver it is felt by some photographers that it is more trouble than it is worth and the use of the recovered "hypo", if such it is, is not undertaken because of its possible injurious effect on the pictures.

When the silver halides, silver bromide especially, is dissolved in "hypo", sodium silver thiosulphate is formed. The solution may contain silver ions and the fact, as we show in this paper, that metals cause a deposition of the silver in a very pure condition is evidence that such is the case.

At this point the investigation was taken up by the junior author. The results, while only of a preliminary nature, are interesting, and we hope to extend the scope of the work at an early date.

After most of the results, here reported, were secured, there appeared in Chemical Abstracts, page 1094, (April, 1924) an abstract of an article in *Chemische Zeitung* by A. Steigmann, describing "A New Method of Precipitating Silver and Gold." In his method the solution of silver halide in "hypo" is treated with sodium hyposulphite $\text{Na}_2\text{S}_2\text{O}_4$, in the presence of soda which reacts with the sulphur dioxide produced during the chemical action. The abstract states that the fixing bath can be regenerated five or six times, but he recommends only

three times. Since the hyposulphite is usually made by reduction of the sulphite with zinc, and since soda must be used to neutralize the sulphur dioxide which is converted into sulphite and this in acid solution, in which the "hypo" is always used, produces sulphur dioxide which might act in an injurious way upon the picture, it seems a more direct and better method to use the zinc directly with the "hypo" in recovering the silver. This would be especially true if, as seems evident from our results, the hypo is as good and safe a fixing agent after treatment with the zinc as when freshly made.

In order to study in a more nearly quantitative way the action of several metals on solutions of silver chloride in ammonia, a nearly saturated solution of the chloride was made and one-half of it was diluted with an equal volume of distilled water. In separate portions of both the concentrated and dilute solutions were placed weighed amounts of the metals, zinc, aluminum, copper and iron and then these were kept in a dark room until all the silver had been precipitated. Before the metals were introduced their surfaces were well cleaned. With all the metals except iron precipitation of silver began at once and all the silver had left the solution within twenty-four hours (the first test was made at the end of this time). In the case of iron in the dilute solution the action had started only slightly at the end of the first hour and was complete only after forty-eight hours. In the concentrated solution the iron remained perfectly bright for the first day, and not a trace of silver had deposited. On being brought into the light, however, action began within fifteen minutes and seemed to continue after it had been replaced in a dark room. When the action had become complete the metals were removed, cleaned and weighed, and the precipitate treated with quite dilute nitric acid. In the case of zinc quite a large amount of material was not dissolved in the acid and appeared like darkened silver chloride. With the other metals only a trace of material was found to be insoluble. In the case of zinc it was found that 54% more went into solution than was equivalent to the silver formed. This might be anticipated from the fact that

water acts slowly on zinc to form the hydroxide. In the case of the other metals the excess loss was not determined.

Since the recovery of silver from "hypo" fixing baths is of commercial importance, most of the time was spent in its study. For this purpose a spent "hypo" solution was obtained from a local photographer. Before using this solution, however, preliminary experiments were performed with a fairly concentrated solution of silver chloride in sodium thiosulphate solution. The method used followed very closely that with ammonia solutions, using the same metals. With all of the metals it was found that the precipitation of silver began very slowly, only after two or more hours, and that it proceeded regularly to completion. With iron the end was reached only after forty-eight hours, but with the others twenty-four were all that was needed. Only slight traces of the precipitate were insoluble in dilute nitric acid. In the case of copper the silver deposited as a smooth layer upon the surface of the copper sheets; with the other metals the silver deposited very smoothly on the glass walls of the containing vessels, forming a mirror more or less perfect.

After this preliminary experiment a liter of the spent liquor, mentioned above, was treated with small rectangular chunks of pure zinc lying at the bottom of the flask. The silver slowly deposited as a mirror on the walls. About four grams of silver were deposited for three grams of zinc disappearing into the solution. This is far less silver than is theoretically possible (3.3 :1), but by using a larger surface of zinc suspended in the solution and by stirring the solution it is believed the amount might be increased nearly to the theoretical.

After the silver had become completely precipitated from the spent liquor a part of it was treated with sodium carbonate to separate the carbonate of zinc. After filtration of the carbonate it was found that the slightly acidified solution (with acetic acid) dissolved 62 grams of silver chloride per liter. The part of the silver-free solution from which the zinc had not been removed was found to dissolve 70 grams of silver chloride per liter.

This would indicate that the zinc salt in the solution had no injurious effect on the solubility of the silver halides, but rather improved it slightly.

In order to test the qualities of the treated "hypo" as a fixing agent the solution from which the zinc had been removed as well as that containing this metal was submitted to an expert student photographer for use in his fixing bath. He reported that both solutions worked in a perfectly normal manner, and that he could observe no decrease in efficiency as compared with the ordinary solution and no difference in the quality of the product.

It is planned to continue the investigation along several related lines and to the end of making the process a commercial success.