

ART. XXIV.—*On some Reactions of Silver Chloride and Bromide*; by M. CAREY LEA, Philadelphia.

IN the course of some examinations made several years since on the reaction of silver bromide and iodide, I concluded that the dark substances produced by the action of light on these bodies are resolved by nitric acid into metallic silver which dissolves, and ordinary silver bromide and iodide, which remain. Since then I have met with a paper by Von Bibra on the reaction of silver chloride, in which that chemist found that darkened silver chloride was not attacked by nitric acid. My previous examination had not included the chloride, and the remarkable difference thus indicated, led me to return to the subject. I found my own previous results entirely confirmed as also Von Bibra's:—at least so far that only by the long continued action of nitric acid was there any decomposition of the darkened chloride, and even then, traces only of silver were taken up by the acid.

It therefore appears that the substance produced by the action of light on silver chloride is of a much more permanent character than in the case of the other silver haloids. Some other reactions noted in the course of the examinations which appear not devoid of interest, are given below.

Silver Chloride.

Our knowledge of the nature of the substances produced by the action of light on the silver haloids is very limited, owing to the fact that although the coloration is very intense, yet the portion of material acted upon is very small. Also because we have no means of removing from the mixture the unaltered haloid, except by agents that at the same time attack the altered substance, and completely change its character.

As to the first point—the small proportion of material actually altered by light. It is generally thought that silver chloride is reduced by the action of light to a sub-chloride containing half

as much chlorine as the normal white chloride. Yet the loss of chlorine has been found too small to be weighed. Fresenius doubts if a loss in weight could be detected by the most delicate balance, and Von Bibra in the investigation above referred to, could not find the slightest loss in weight.

With a view to obtain some quantitative indication in the matter, the following determination was made.

Silver chloride was precipitated with an excess of hydrochloric acid, was well washed, and exposed to bright sunlight for five days. During this time it was spread in a very thin layer over the bottom of a large white porcelain basin, was frequently stirred up to bring constantly new surfaces to the light, and was kept moistened with water.

Of the resulting dark powder two grams were taken and were thoroughly treated with sodium hyposulphite to remove the unaltered chloride. Previous experience had shown that extraordinary precautions were necessary to effect this thoroughly, as the removal of the last portions of normal silver chloride is very difficult. Accordingly the strong solution of hyposulphite was many times renewed, each time being left to act for from twelve to twenty-four hours. Finally the gray residue (metallic silver) was washed, dried and weighed, and found to amount to twenty-one milligrams.

It thus appears that as the result of five days' action of strong sunshine, with frequent stirring up and mixing to bring fresh portions to the light, about one per cent only of the silver chloride was acted upon. And if we suppose this action to consist in removing one-half the chlorine, then the whole loss in weight by the action of the light should be but little over one-tenth of one per cent. This proportion is of course not inappreciable, and the observations of Fresenius and of V. Bibra above quoted must be taken as referring to shorter exposures.

It was mentioned that another difficulty in verifying the nature of the action of light lay in the fact that those substances which can be used for dissolving out the unaltered chloride, also unfortunately attack the altered substance.

The two reagents most effectual for this removal are sodium hyposulphite, and liquid ammonia. That they also alter the blackened portion is at once evident from the fact that the residue which they leave behind instantly dissolves in cold nitric acid of sp. gr. 1.28 with evolution of red fumes, and is in fact, well known to be metallic silver, whereas before the application of these reagents, cold nitric acid has no effect, and even with boiling acid, applied for a long period only very slight decomposition ensues.*

* The facts here mentioned lead to the curious reflection that the permanency of ordinary photographic prints is greatly diminished by the fixing process. For in this fixing process which consists in immersion into solution of sodium hyposul-

When cold nitric acid, sp. gr. 1.28, is poured over a quantity of the darkened chloride (precipitated with excess of HCl) and left to remain for a time in contact, this acid acquires no silver reaction whatever. It is therefore certain that by the action of light on silver chloride (precipitated in presence of excess HCl) *no metallic silver is reduced*. And as this black substance is quickly whitened by aqua regia, it is reasonable to conclude that the dark matter contain less chlorine than the normal, and is either a subchloride or an oxychloride. Beyond this, we know nothing with certainty.

When the dark substance was boiled for several minutes with the same nitric acid, no silver was extracted. But when the vessel was placed on a sand bath and kept at or near boiling point for eighteen hours, renewing the acid as it escaped, a distinct effect was produced. The substance became a little lighter in color, and the acid was found to have taken up enough silver to show a strong opalescence by addition of hydrochloric acid; not enough however to give an immediate precipitate.

Ammonia and sodium hyposulphite have this in common, that both leave metallic silver behind when the darkened chloride is submitted to their action. In the case of the sodium salt, it is of course understood that it is presented in strong solution and very large excess.

Silver Bromide.

Silver bromide was precipitated with excess of KBr and well washed, and exposed to light.

When cold nitric acid, sp. gr. 1.28, was allowed to stand for one minute over the darkened bromide it took up silver abundantly. Allowed to act for an hour at a heat considerably below 212° the color of the darkened bromide had considerably changed and at the end of seven or eight hours, complete decomposition had taken place. The resulting AgBr is lemon yellow and has more the general appearance of iodide than of bromide.

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phite, an exceedingly stable substance which almost completely resists the action of boiling nitric acid is reduced to metallic silver, in the condition of a thin layer of almost infinitesimally fine particles, and in that condition not well able to resist external influences. To a considerable extent this difficulty is obviated by a partial substitution of gold for the metallic silver.

The use of a fixing treatment can of course never be dispensed with, as it is essential to remove the unaltered chloride. But it is evident that if a substance could be found which would remove the unaltered chloride only, without attacking that which has been darkened by light, a great advantage would probably be gained. The gold treatment could be dispensed with, the printing could be stopped when the right strength was obtained, without being carried further to allow for the weakening effect of the fixing agent, and the print obtained would probably be always perfectly permanent.

The fact that both sodium hyposulphite and ammonia in removing the unaltered chloride, reduce the altered to metallic silver, explains why the gold toning operation succeeds much better when applied after the fixing operation, than before it.