The Chemistry of Photography.*

By J. R. Burn.

Photo chemistry is really the study of all those chemical changes which are brought about by light when it is absorbed by various substances, and its energy is expended in producing chemical decompositions; but I intend only to speak of it in its relations to the art of photography, and would more correctly have styled this paper with the longer title of "Photographic Chemistry."

The practical illustrations will be necessarily few, and limited to those which can be performed in gaslight, as some of the most interesting and instructive require a non-actinic light and considerable time to perform.

The chemistry of photography encroaches largely upon the domain of physics, perhaps more so than any other branch of chemistry, since nearly all the decompositions involved are at least initiated by the action of light.

The dictionary (Nuttall's) definition of photography is: "The art of fixing images of the *camera obscura* on plates of copper covered with a thin coating of silver." This definition takes us back to the days when photography was in its infancy, in the early part of the present century, since which time the term has come to mean a great deal more; but one point still holds good, and it is this, that all the surfaces employed for obtaining the image in the camera, almost without exception, are still dependent for their efficiency upon the susceptibility of silver salts to the action of light.

I will give but a short sketch of the history of photographic chemistry. Color photography was taken as a subject in a paper on "Recent Advances in Photography," by Mr. E. W. Hill, before the London Chemists' Assistants' Association, in November last, but I will refer to the chemistry of color photography, or, rather, orthochromatic photography, later on under orthochromatic plates.

History.—The action of silver nitrate in darkening the skin is reported as having been noticed as far back as the thirteenth century by Albertos Magnus. In the sixteenth century Fabricius mentioned the fact that horn silver, or native silver chloride, turned darker in color when removed from the mines, and the discoloration of silver compounds was noted by Glauber and Robert Boyle in the seventeenth century, but they do not appear to have attributed this change to the action of light. Schülze, a German physician, appears to have been the first to definitely prove that light and not heat, or action of the air alone, was the cause of the darkening, and he showed it experimentally by pouring silver dissolved in nitric acid upon chalk, and observing that the precipitate darkened upon the side exposed to light. It was not till the middle of last century that it was noticed by Professor Beccerues, of Turin, that precipitated silver chloride turned violet, then brownish violet, on exposing to light, and it is on a similar change in the chloride, bromide, and iodide of silver, that the principal photographic processes of the present time depend. Two or three simple experiments here will serve to indicate what occurs when the halogen silver salts are exposed to the action of light, and will make my subsequent remarks much clearer.

Experiments.—The first experiment is intended to show the change of color in silver chloride by exposure to light. I form a precipitate of silver chloride in two large test tubes by adding to a solution of silver nitrate some hydrochloric acid. Above each precipitate I suspend bibulous paper moistened with potassium iodide and starch paste, then expose one of the tubes to the light of an electric arc for a few minutes while the other is kept in the dark. It will be noticed that the precipitate has changed color, from white to violet, in the tube exposed to light; also that the paper above it turns blue, indicating that chlorine, or some chlorine-containing gas, has been liberated, while that retained in the dark remains apparently unchanged. This clearly shows that the AgCl has, to some extent, been reduced by the action of light.

Next I form another quantity of silver chloride, pour upon it strong nitric acid, and expose to the electric light (gaslight is not sufficiently actinic or chemically active to serve the purpose) as before, and it will be seen that the change still takes place, although nitric acid is one of the strongest oxidizing agents. I will refer to this later.

At this point I must explain what is meant by the terms "sensitizers" and "restrainers." Any substance which, by its presence and chemical or physical action, causes the reduction of the silver salt by light or a developer to take place more easily and rapidly is called a "sensitizer"; while any substance which, by its presence, retards or prevents the chemical decomposition of the silver or other salt acted upon is known as a "restrainer."

In illustration of restrainers, I have some silver nitrate solution as before, and add to it some gelatine solution, then a few drops of hydrochloric acid. It will be observed that the precipitate is much slower in forming, and this is because the gelatine, by giving viscosity to the solution, acts as a "physical restrainer," yet, at the same time, gelatine is used as a "chemical sensitizer," because it has the power, even when "set," of absorbing the halogen-chlorine, bromine, and iodine.

Collodin is also a "physical restrainer," but it differs from gelatine in that it is not a "chemical sensitizer," *i.e.*, it will not absorb or combine with the halogen.

Ferrous sulphate is used as a developer for collodion wet plates, and acts by reducing the silver nitrate to the metallic state, while the ferrous salt is raised to the ferric condition according to this equation:

$$6FeSO_4 + 6AgNO_3 = 2Fe_2(SO_4)_3 + Fe_2(No_3)_6 + 3Ag_2.$$

On performing this experiment in test tubes it is seen that the reaction takes place at once, and it is too rapid to be of service in development, but on doing this again in the presence of a little acetic acid it is evident that the reaction takes place much more slowly. It is thus that acetic acid acts as a "chemical restrainer" in development.

After this digression, I will now refer briefly to the more important processes in the order of their discovery which have led up to our present state of knowledge in the art of photography. The first process of copying pictures painted on glass, or profiles cast by a strong light, was devised by Thomas Wedgewood and Humphry Davy in the year 1802, and was performed by placing the transparent picture or the opaque profile in front of paper or leather impregnated with solution of silver nitrate or coated with silver chloride, and exposing to light. A darkened image was produced, but they had no means of fixing this image, *i.e.*, preventing a further darkening of the silver salt by what we call a fixing agent, and consequently the result was not permanent. This is, of course, quite similar to our methods of printing in the printing frame. An imperfect fixing agent was supplied by Fox Talbot, in 1839, who employed a solution of common salt, which acted by removing the greater portion of the silver chloride which had not been acted upon by light, but not all, therefore the resulting picture was not permanent. In the same year Sir John Herschell showed how all the unaltered silver salt might be dissolved by sodium thiosulphate, or "hypo," which is the fixing agent still most generally employed. The prints were called Talbotypes, after Fox Talbot. Joseph Nièsse, in 1824, was the first to be successful in fixing a photographic image obtained by means of a lens, and he did this by coating a metallic plate with bitumen, a pitch like substance, and exposing in a camera for *some hours*. His developer was a rather expensive one, viz., oil of lavender, which dissolved the portions of bitumen unaffected by light, and left on the plate a picture of insoluble bitumen. Nièsse discovered this method after working on various substances for a period of fifteen years. Nièsse died in 1833, and in 1839 Daguerre, who worked along with Nièsse a few years before he died, made known what is called a Daguerreotype process. In this process a highly polished plate of silver, or silvered copper, is exposed to the vapors of iodine and bromine alternately, forming a film of silver bromo-iodide, the sensitiveness being judged by the color of the surface. The method of sensitizing was improved until a Daguerreotype plate was prepared, which is as rapid as a wet collodion plate, but the image can only be seen at a certain angle.

The Calotype process, which comes next, was patented by Fox Talbot in 1841, and consists in having a mixture of bromide and iodide of silver on paper

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