

XI.—*On the preparation of the Prussian Blue, generally known as "Turnbull's Blue."* By ROBERT WARINGTON, ESQ.

In bringing the present notice before the Society, I feel it necessary to apologise for introducing a subject to their attention which has been so ably investigated by many of our most eminent chemists, and the results of whose labours are to be found in the Chemical Manuals of the present day. Yet, when we find substances in commerce, under this title, or under the various magnified appellations of "Egyptian blue," "Cerulean blue," &c., differing exceedingly in character from each other, some of them of great beauty in colour, and frequently possessing modified properties; when the difficulty attending the preparation of this blue of an uniform tint, which is a great source of annoyance to many of the makers, is also taken into consideration, I am induced to believe that the results of the investigation may not be deemed uninteresting to the Members of this Society, or unimportant to the manufacturing chemist. The greater part of the experiments were made in the year 1834, and many of them have been lately repeated, the investigation has also been extended, for the purpose of confirmation, before being submitted to the Society.

I must premise, that the great object in view in commencing this investigation, was the production of a colour analogous to what was then known as "Turnbull's blue," and was, at the period I allude to, made, I believe, only by the firm of Turnbull and Ramsay, of Glasgow; its extreme beauty, and the bright, metallic, coppery lustre exhibited on its surface, will be well known to most of our Members. I need hardly say that numerous unsuccessful experiments were made before anything approaching the desired tint was obtained. Its attempted production from a persalt of iron by various and modified processes was unsuccessful in every case; nothing comparable with it in lustre or beauty was obtained. After trying the different persalts of iron, the method of peroxidizing the protosalt was varied, and this was followed by the action of the ferridecyanide of potassium on the protosalt, in place of the ferrocyanide on the persalt, but the result was still not perfectly satisfactory.

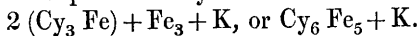
In the course of these experiments, however, certain points were noted, which ultimately led the way to the desired result; one of the principal of these, and that which bears most fully on the present subject, was the fact, that the precipitate produced by a solution of the ferrocyanide of potassium in the solution of a protosalt of iron, has a most powerful affinity for oxygen; every one must be aware of this to a certain extent, inasmuch as the precipitate absorbs oxygen from the air, and becomes deepened in colour; but so energetic is this attraction, that many solutions of the salts of metallic oxides are deoxidized rapidly and perfectly when brought within the sphere of its action; many of the blue salts of copper are rendered colourless, salts of chromic acid are reduced to salts of the green oxide, sufficient acid being present to hold in solution the protoxide of chromium which is produced; salts of peroxide of tin, mercury, and iron are also rapidly reduced to the state of protosalts.*

The precipitate, in either of these cases, darkens and becomes gradually of a deep blue colour, which is more or less intense as the quantity of the metallic salt, or the proportion of oxygen contained in it, varies; the fine, metallic, coppery lustre is at length gradually developed. As this effect could thus be produced by salts of a metallic oxide, there was no apparent reason why the same result should not be arrived at with solutions of other agents containing oxygen either in large quantity or feebly combined, as for instance, in chloric acid and its salts, and in chlorous acid.

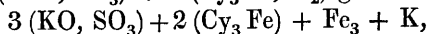
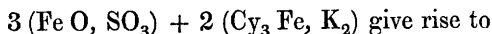
Another point was also rendered evident from the above experiments, namely, that it was actually necessary that the precipitate formed in the protosalt of iron by ferrocyanide of potassium should first be produced in order to obtain the state of molecular aggregation in the compound capable of yielding a blue of the fine colour and lustre sought, and upon which, as a basis, the effect of oxidizing agents could be fully developed. The composition of this precipitate,

* I may mention here that this re-action with the salts of iron affords an excellent means of securing a solution of this metal in the state of protoxide for the purpose of exhibiting its peculiar reactions in the Class-room, experiments which are at times attended with some little annoyance. For this purpose a solution of the ordinary protosulphate of iron is to be partially precipitated, in a well-corked or stoppered bottle, by a solution of the ferrocyanide of potassium, and the precipitate allowed to subside; it will then be found that this precipitate has reduced the remaining part of the solution to the state of protosulphate most perfectly, and that this is now capable of yielding a pure white precipitate, both with solutions of the carbonated alkalies and with additional solution of the ferrocyanide of potassium. The same effect may be produced by adding a portion of the recently precipitated ferrocyanide of iron to a solution of sulphate of iron.

or white Prussian blue, has been pretty well ascertained by numerous investigators and is represented by the formula :



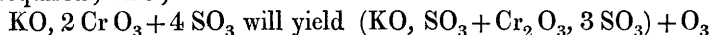
It is produced by the action of two equivalents of the ferrocyanide of potassium upon three equivalents of the protosulphate of iron ; thus :



or sulphate of potash and the white Prussian blue.

Now the question arises, as to what chemical action takes place during the darkening in colour or oxidation of this compound through the medium of oxidizing agents, and I shall presently be able to show, that it is the conversion of the equivalent of potassium, which forms one of its ingredients, into potash, and the removal of the potash at the same time, by the agency of an acid, with which it is able to combine. I have already shewn that there are various agents by which this oxidation may be effected ; those which I have found to answer the purpose most efficiently, are : 1st. the bichromate of potash ; 2nd. the chlorate of potash ; 3rd. a soluble persalt of iron ; 4th. chlorinated soda, or a solution of chloride of lime.

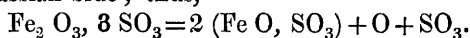
When bichromate of potash is employed, it is necessary to use one-third of an equivalent only, as the salt will afford three equivalents of available oxygen, and to effect our object perfectly, one only is required ; thus,



or one equivalent of bichromate of potash treated with four equivs. of sulphuric acid, will give rise to one equiv. of sulphate of chromium and potash (chrome alum) and three equivs. of oxygen, and as the single equivalent of potassium we wish to oxidize requires only one equiv. of oxygen, the third part of an equiv. of the bichromate will suffice for our purpose ; an additional equivalent of sulphuric acid is, however, indispensable for the purpose of uniting with the potash resulting from this oxidation.

When chlorate of potash is used as the oxidizing agent, about one-fifth of an equivalent is sufficient for the oxidation, the requisite proportion of hydrochloric acid being added to decompose the salt, and set the chloric acid free ; as in the former case, care must be taken that an equivalent of sulphuric acid is present, to combine with the resulting potash. The same remarks will equally apply to the employment of chlorinated soda or chloride of lime ; the latter compound, however, is objectionable from the sulphate of lime which is necessarily produced when protosulphate of iron or

sulphuric acid is made use of in the operation. In the third case, where a persalt of iron is the oxidizing medium, and in these experiments I have always employed the persulphate, the preparation of which will be immediately described, a single equivalent is necessary to yield the one equiv. of oxygen, and sufficient sulphuric acid is contained in this solution to combine with the oxidized potassium after the iron has been reduced to the state of protoxide by the action of the white Prussian blue; thus,



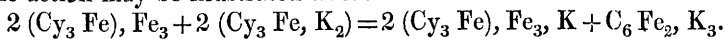
That this action is owing to the oxidation and subsequent removal of the equivalent of potassium, will, I think, be evident from the fact, that when the bichromate of potash is employed in the proportion stated, the supernatant liquor has the pinkish-blue colour of the double sulphate of chromium and potash; but if more than this be used, a portion of bichromate remains in solution, exhibiting its characteristic orange-colour. The same remarks apply to the persalt of iron, any excess above the equivalent required, being found in the filtrate or supernatant liquor when the Prussian blue has subsided.

To prepare the persulphate of iron, I have found that either bichromate of potash or chlorate of potash may be employed with much greater advantage than nitric acid; care must be taken that sufficient sulphuric acid is present to hold the peroxide of iron produced in solution; and also, in the first case, to form chrome alum with the deoxidized chromic acid; the decomposition of the chlorate of potash should always be effected by hydrochloric acid. Now as the protosulphate of iron assumes an additional half equivalent of oxygen to form persulphate, it will be evident that one-sixth of an equivalent of bichromate of potash, or one-tenth of an equivalent of chlorate of potash with the requisite proportion of acid will be sufficient for this conversion. When the oxidizing solution is prepared with chlorate of potash, the solution, after the oxidation of the white Prussian blue, may be precipitated by ferrocyanide of potassium for a future operation; if bichromate has been used, the protoxide of chromium will, to a certain extent, be precipitated by the ferrocyanide of potassium, and interfere with the brilliancy of the subsequent colour.

The white Prussian blue should be precipitated from dilute solutions in order to obtain an uniform product in the proper state of aggregation. I find that when the materials are respectively dissolved in about ten times their weight of water, a very good result is obtained.

It is well known that when Turnbull's blue is digested in a

solution of the ferrocyanide of potassium, a pale or white Prussian blue and ferridecyanide of potassium result ; this is best effected by acting on one equivalent of the former with two of the latter, and the action may be illustrated thus :



The result being one equiv. of the white Prussian blue, and one equivalent of ferridecyanide of potassium.

March 21, 1848.

The President in the Chair.

Dr. Edward Schunk presented his Essay "On Madder" to the Library.

Messrs. F. A. Abel, Thomas H. Rowney, and Robert Richardson were duly elected Members of the Society, and Messrs. Robert Murray and J. G. Latta as Associates.

The following papers were read :