

This paper is in a collection of

**“Historic Publications in Electrochemistry”**

which is part of

**Electrochemical Science and Technology Information  
Resource (ESTIR)**

(<http://electrochem.cwru.edu/estir/>)

*Bas*

*Wilson Annex*

*QD1*

*.C52*

*V.15*

*1862*

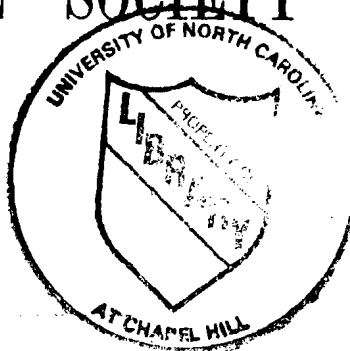
THE  
JOURNAL

OF

THE CHEMICAL SOCIETY

OF

LONDON



Committee of Publication.

E. FRANKLAND, PH.D., F.R.S. | W. OBLING, M.B., F.R.S.  
A. W. HOFMANN, L.L.D., F.R.S. | A. W. WILLIAMSON, F.R.S.

VOL. XV.

LONDON  
BUTTERWORTHS SCIENTIFIC PUBLICATIONS LTD.  
1950

XXIX.—*On the Production of a Blue Substance by the Electrolysis of Sulphate of Aniline.*

By H. LETHEBY, M.B., M.A., Ph.D., &c.

[Professor of Chemistry in the College of the London Hospital.]

HAVING had to investigate two cases of fatal poisoning by nitrobenzol, and finding that this compound is changed in the living stomach into aniline, I was led to enquire into the chemical reactions of this alkali, in the hope of discovering a delicate and certain test for it. That which first commanded my attention was the fact, that a salt of aniline, under the influence of nascent oxygen, from any source, acquired a blue or purple colour. But the reactions were not in all cases equally delicate, a  $\frac{1}{1000}$  of a grain of aniline in half a drop of dilute sulphuric acid (1 to 1) gradually became blue when treated with a little peroxide of lead, or red prussiate of potash, but it required about double this quantity of aniline to show the blue or purple reaction with peroxide of manganese or bichromate of potash; and it was hardly possible to bring out the distinctive colours with less than the  $\frac{1}{100}$  part of a grain, with peroxide of hydrogen, peroxide of barium, chlorine or chloride of lime. Referring to my original experiments with strychnine, in which I found that a sulphatic solution of the alkaloid was instantly coloured deep blue, when placed upon a strip of platinum and brought under the influence of the nascent oxygen from the positive pole of a galvanic battery, it occurred to me that the same mode of manipulation with aniline would be attended with a like result. I therefore took a little of the alkali and dissolved it in dilute sulphuric acid (about 1 to 1), and placed a single drop of the solution on a strip of platinum; the platinum was brought into contact with the positive pole of a small Grove's battery (3 inches by 2), and the solution was touched with the negative pole. Instantly the liquid acquired a purple and finally a pinkish colour. This

reaction was distinct and very fully characteristic when only the  $\frac{1}{2000}$  of a grain of aniline was used. It was, therefore, by far the most delicate of all the nascent oxygen tests for the alkali.

In the course of my medico-legal enquiries, however, I found that, with strong solutions of the alkali, the colour was not violet but deep blue, and sometimes greenish blue, and that the pigment adhered as a fine powder to the platinum. It occurred to me, therefore, that it would be interesting to procure this pigment in a somewhat large quantity in order that its nature might be ascertained. About two ounces of aniline were dissolved in dilute sulphuric acid, and placed in a large beaker. It was then brought under the electrolytic action of two sets of Grove's batteries (each 6 inches by 4) arranged for intensity. A sheet of platinum 6 inches by 4 was placed in the aniline solution and brought into contact with the positive pole of the battery, a flat porous cell containing dilute sulphuric acid was also placed in the solution, and this was connected by a similar sheet of platinum with the negative pole of the battery. By this arrangement, the nascent hydrogen from the negative pole was kept apart from the aniline solution, so that the nascent oxygen from the positive pole might have free and undisturbed action on the aniline. Very soon the positive sheet of platinum became covered with a thick layer of dirty bluish-green pigment. This was removed, and, after being well washed with water, was collected in a filter and dried. Its leading properties are as follows:—

It occurs in the form of a dirty bluish-black powder, which is insoluble in water, alcohol, ether, ammonia, &c. While it rests on the platinum, it acquires a brilliant blue colour by immersion in ammonia, but the blue pigment does not dissolve.

Concentrated sulphuric acid dissolves it, and forms a blue, a green, or a violet solution according to the degree of concentration; and when the solution is diluted with water, a dirty emerald green powder subsides. This is also made blue by concentrated ammonia, and blue or purple by concentrated sulphuric acid.

The blue pigment is partly decolorized by reducing agents, or lime and sulphate of iron; and in this condition it dissolves, and, like indigo, acquires a blue colour on exposure to the air.

The dry pigment is decomposed at a red heat, evolving water and sulphurous acid, and leaving a black cinder.

The composition and chemical reactions of the pigment are now being investigated by Mr. Fewtrell and myself, and will be here-

after the subject of communication to the Society. The present note is merely intended as an exposition of the fact, that a blue pigment is produced by the electrolytic oxidation of a sulphatic solution of aniline.

---