

**THE CHEMICAL HISTORY
AND PROGRESS OF
ANILINE BLACK**

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The chemical history and progress of aniline black by John Lightfoot

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JOHN LIGHTFOOT

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CHEMICAL HISTORY AND PROGRESS
OF
ANILINE BLACK.

BY
JOHN LIGHTFOOT, CHEMIST.



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P R E F A C E.

THE object of the present pamphlet is to give to the Chemists and others connected with Dyeing and Calico Printing, the true History and Progress of Aniline Black during the past ten years, as well as some curious experiments made with the purpose of determining many vexed and debated points in connection therewith.

As the inventor and first producer of the Aniline Black upon calico, I have naturally wished to overcome any difficulties in using it, and to add from time to time to our information of its properties, and the mode of its formation.

Up to the present time, no very certain or well-defined theory has perfectly accounted for this product of Aniline; and if my experiments will not even now explain it, I may at least hope to add to the amount of knowledge we already possess upon this permanently fast black.

JOHN LIGHTFOOT.

LOWER HOUSE, BURNLEY,

May 1, 1871.

ANILINE BLACK.

IN the year 1859, I was working out some experiments upon aniline for Mr. Richard Dugdale Kay, of Accrington, which he had sent to me as oil of naphtha; the market price of it was then from 15s. to 20s. per lb.

In November, of the same year, I found that by mixing an acid chloride of aniline (equal parts of pure hydrochloric acid and aniline) with starch paste, holding 4 ozs. of chlorate of potash per gallon, and printing the mixture with a wood block, that little or no colour was produced after twenty-four hours' ageing; but that when the same colour was printed in the machine with the copper roller, a green colour was produced in twelve hours.

My notice of this strange fact was the cause that led me to the discovery of the aniline black. I at once repeated this mixture, and added to it various proportions of nitromuriate of copper, 88° T., and I then found that the intensity of the black was dependent upon the proportions of copper and aniline salt employed, as well as the duration of the ageing.

The colour, when first printed, was a pale olive, which gradually developed into the fibre to an intense myrtle green, in about twenty-four hours. When washed in water *only*, without alkali or soap, it became an intense black.

Subsequent experiments of M. Rosentheil and others have proved that the mixture of chloride of aniline, starch paste, and chlorate of potash, made in an earthen vessel, does not give much colour if printed with a wood block.

The colour I made was mixed in a copper vessel, and this, with the copper rollers, gave me the dark green that I printed in November, 1859; but the true black itself was not produced until the salt of copper was added to the mixture.

The high price of aniline at this time prevented me thinking much of the black, except as a chemical curiosity; but I had sufficiently developed the colour to print a few pieces of calico in July, 1860, at the Broad Oak Print Works, Accrington, from the following mixture:—

| | |
|---|-----------|
| Starch paste (1½ lbs. per gallon) . . . | 1 gallon. |
| Chlorate of potash | 4 ozs. |
| { Aniline (oil of naphtha) | 8 " |
| { Hydrochloric acid, 32° T. | 8 " |
| Sal ammoniac | 4 " |
| Nitrate of copper, 88° T. | 2 " |

This colour was printed with madder pink ground, aged two nights; then the black and pink passed through "Higgins'" alkaline arseniate of soda, mixed with water at 180° F., washed, dunged, dyed in madder, and soaped.

Except a few pieces of single blacks, nothing more was done till the end of the year 1862, when an offer was made for the process by Messrs. J. J. Müller and Co., of Basle, Switzerland, which resulted in it being patented in January, 1863, and sold to them.

My own personal account of the share I had in the discovery may be concluded with the following correspondence from the "Chemical News":—

"'Chemical News,' December 6, 1862.

"BLACK DYE FROM ANILINE.

"*To the Editor of the Chemical News.*

"SIR,—There have been many colours produced from 'aniline' and its analogues, namely, violets, pinks, blues, etc., but I have not seen or heard of a good black that has been produced from aniline, capable of being printed or dyed along with the above-named colours, excepting one that was discovered by me about two years ago; and I now take the opportunity of enclosing you swatches of my new black from aniline (dyed and printed) for your inspection and trial.

"This black has peculiar properties, being perfectly fast, and not affected either by light or being boiled for several hours in a strong

solution of soap. Strong sulphuric acid destroys the cotton, but leaves a black or purple pigment behind. Strong caustic soda does not injure the colour, even if boiled, and the strongest solution of hypochlorite of lime does not affect it in the least; in fact, all the chemical agents I have tried will not discharge it. It is a valuable black for Turkey-red styles; and when printed along with madder colours it fixes 'perfectly fast,' and does not take the dye from the madder-bath; hence its value as a substitute for chemical black. It is also valuable as an 'indelible ink,' and for marking grey goods, as a substitute for 'tar.'

"If you will kindly insert this in your next journal, perhaps some of your numerous correspondents will suggest some other use for this 'indestructible black.' I simply bring this before your notice, lest it should be claimed by some other colourist or chemist at some future time.

"I am, etc., "JOHN LIGHTFOOT.

"Broad Oak Laboratory, Accrington, Lancashire.

"[The colour is not a pure black, and does not look so well in the solid as in the printed specimens, which show extremely well. Chlorine will almost discharge the colour.—ED. C. N.]"

NOTE.—C. Kœchlin has since noted the fact that, though apparently discharged by chlorine, the black returns in all its intensity in a few days.

"'Chemical News,' December 20, 1862.

"BLACK DYE FROM ANILINE.

"*To the Editor of the Chemical News.*

"SIR,—Having seen a notice of a new black from aniline in a recent number of the 'Chemical News,' I would state, that some time ago I obtained on cotton fabric a black from aniline, capable of resisting acids, alkalies, and other re-agents to a very remarkable extent, and which was very difficult to discharge.

"I am, etc., "W. CORT WRIGHT.

"Laboratory, Bank Bridge, near Manchester."

"'Chemical News,' January 3, 1863.

"BLACK DYE FROM ANILINE.

"*To the Editor of the Chemical News.*

"SIR,—In reply to a notice in the 'Chemical News' of Decem-

ber 20, 1862, and signed by Mr. W. Cort Wright, I beg to say that I have seen a black from aniline, dyed and printed in July, 1860, which was discovered by Mr. John Lightfoot, jun., Broad Oak Print Works, Accrington, a swatch of which I beg to enclose.

"I am, etc., "J. C. DERBYSHIRE.

"Church, near Accrington."

[M. Emile Gatty preserved a specimen of this black, printed and given to him in 1860, and returned it to me in 1863.]

The following patents, more or less connected with the history of the aniline black, are given in their chronological order. Only so much of their subject matter, in the less important ones, is indicated as is necessary to understand the remarks attached to them:—

Almost the earliest, if not *the* earliest, mention of aniline black, will be found in the patent of

Dale and Caro, 1860, 26th May, No. 1,307,

for "obtaining colouring matters of purple and red shades from pure or commercial aniline."

Salts of aniline, mixed with solutions of perchloride of copper, were heated, which gave a "black or dark purple precipitate." The purple colouring matter is extracted, first with hot water and then with alcohol, "until the whole of the purple colouring matter has been dissolved out."

The patent does not expressly mention the black residue left from the washings, but the black residue has for a long time been sold by Messrs. Roberts, Dale and Co., of Manchester, under the name of "Aniline Black Pigment." It is, perhaps, the best black known for "topical" printing with albumen colours, as it does not tarnish the "ginguets green," or "ultramarine blue," *like the logwood black.*

Calvert, Lowe and Clift, 11th June, 1860, No. 1,426.

Patent for "the production of a green insoluble colouring matter from aniline, by oxidation directly in contact with the yarn tissue or fabric," termed "emeraldine," and the "conver-