

UNITED STATES PATENT OFFICE.

RENÉ BOHN, OF MANNHEIM, GERMANY, ASSIGNOR TO THE BADISCHE ANILIN AND SODA FABRIK, OF LUDWIGSHAFEN, GERMANY.

BLUE-BLACK DYE AND PROCESS OF MAKING SAME.

SPECIFICATION forming part of Letters Patent No. 609,327, dated August 16, 1898.

Application filed December 27, 1897. Serial No. 663,722. (Specimens.) Patented in Germany November 23, 1895, No. 88,236, June 14, 1896, No. 92,471, August 18, 1896, No. 92,472, and August 20, 1896, No. 92,538; in France April 10, 1896, No. 255,452, and in England April 13, 1896, No. 7,766, and September 12, 1896, No. 20,250.

To all whom it may concern:

Be it known that I, RENÉ BOHN, doctor of philosophy, a citizen of the Swiss Republic, residing at Mannheim, in the Grand Duchy of Baden and Empire of Germany, have invented new and useful Improvements in the Manufacture of new Blue to Black Coloring-Matters from Dinitronaphthalene, (for which patents were obtained in Germany November 23, 1895, No. 88,236, June 14, 1896, No. 92,471, August 18, 1896, No. 92,472, and August 20, 1896, No. 92,538; in England April 13, 1896, No. 7,766, and September 12, 1896, No. 20,250, and in France April 10, 1896, No. 255,452, and August 31, 1896, No. 255,452, certificat d'addition,) of which the following is a specification.

My present invention relates to the direct production of new water-soluble coloring-matter for wool, which is violet blue to blackish in deep shades, by suitable reduction from 1.1' dinitronaphthalene or from the technical product which contains varying quantities of 1.4' dinitronaphthalene by the aid of alkaline solutions of the sulfites, (using the term "sulfites" to include ordinary sulfites or bisulfites of the alkalies or the alkaline earths.) In these solutions the 1.4' dinitronaphthalene is less easily dissolved than the 1.1' dinitro body, so that by interrupting the operation at a suitable point and filtering practically the same product is obtained as if the pure 1.1' dinitro body had been used as initial material. The said violet-blue to black coloring-matter for wool results from the reduction of the solutions of the dinitronaphthalene in alkaline solutions of the sulfites or bisulfites of the alkalies or alkaline earths with suitable reducing agents—for example, sodium sulfid, grape-sugar, milk-sugar, sodium stannate, zinc-dust, or the like.

This invention is best illustrated by the following examples; but the invention is not confined to the methods, proportions, or the like given in the examples. The parts are by weight.

The Production of a New Violet-Blue Coloring-Matter A from Pure 1.1' Dinitronaphthalene.

Example I: Ten (10) parts of finely-ground

1.1' dinitronaphthalene, five hundred and ten (510) parts of water, twenty (20) parts of sodium sulfid, ($\text{Na}_2\text{S} + 9\text{aq.}$) twenty (20) parts of sodium-bisulfite solution of 39° Baumé, and twenty (20) parts of caustic soda-lye of 30° Baumé are kept at a temperature of eighty degrees centigrade (80° C.) until no unchanged dinitronaphthalene remains. The solution is now treated with hydrochloric acid and boiled as long as sulfurous acid is given off. The coloring-matter is now precipitated with sodium or potassium chlorid, filtered, washed with a solution of sodium or potassium chlorid, and dried. The product so obtained is a violet-black powder of metallic luster, which dissolves in cold water, giving a pure violet solution. From an acid-bath it dyes unmordanted wool in violet-blue shades. This coloring-matter is insoluble in alcohol, almost insoluble in anilin, gives a pure-blue solution with ammonia-water, a blue-green solution with caustic-soda solution, a blue-green solution having a green fluorescence with sulfuric acid of 66° Baumé, and a green-blue solution with fuming sulfuric acid containing twenty-three per cent. of free anhydrid.

Example II: The same result as is obtained in Example I may be reached when working as follows: One hundred (100) parts of finely-ground 1.1' dinitronaphthalene are boiled with five hundred (500) parts of sodium-bisulfite solution of 39° Baumé, one hundred and fifty (150) parts of caustic soda solution of 30° Baumé, and one thousand (1,000) parts of water until all the dinitronaphthalene has been dissolved. Then one hundred and fifty (150) parts of sodium sulfid ($\text{Na}_2\text{S} + 9\text{aq.}$) are added and the temperature kept at ninety-five degrees centigrade, (95° C.) the mixture being stirred until the color has become a beautiful deep blue. The mixture is now acidified with four hundred (400) parts of hydrochloric acid, containing 30 per cent. real HCl. The coloring-matter is precipitated by common salt or potassium chlorid and alcohol. The properties of the product so obtained are the same as those of the product of Example I.

Example III: Ten (10) parts of finely-ground 1.1' dinitronaphthalene, eight hundred (800) parts of water, ten (10) parts of

grape-sugar, twenty (20) parts of sodium-bisulfite solution of 38° Baumé and twenty (20) parts of caustic-soda solution of 30° Baumé are kept at a temperature of eighty (80°) degrees centigrade until no unchanged dinitronaphthalene remains. This requires about two (2) hours. The solution, which has now become of a beautiful blue color, is treated with thirty (30) parts of hydrochloric acid of 20° Baumé and boiled until sulfurous acid is no longer given off. The coloring-matter is now precipitated by sodium or potassium chlorid, filtered, pressed, and dried. The properties of the product are the same as those of the product of Example I.

2. *From the Commercial 1.1' Dinitronaphthalene Containing 1.4' Dinitronaphthalene.*

Example IV: Proceed as in the foregoing Example II, heating, however, only until the 1.1' dinitronaphthalene has been dissolved and filter from the unchanged 1.4' dinitronaphthalene. The filtrate is then worked up in the same way as is there described for the solution of 1.1' dinitronaphthalene. The product so obtained is the same as the one obtained in the preceding examples.

30 *The Production of a Violet-Black to Black Coloring-Matter from a Mixture of 1.1' Dinitronaphthalene and 1.4' Dinitronaphthalene.*

Example V: Two hundred (200) parts of grape-sugar are dissolved in seven hundred and fifty (750) parts of water and treated with four hundred (400) parts of sodium-bisulfite solution of 38° Baumé and two hundred (200) parts of caustic-soda solution of 30° Baumé. Two hundred (200) parts of finely-ground dinitronaphthalene, containing about eighty per cent. of 1.1' dinitronaphthalene and about twenty per cent. of 1.4' dinitronaphthalene, are introduced into this solution at ordinary temperature. The whole is now slowly warmed up to seventy-five degrees centigrade (75° C.) and kept at this temperature for about five (5) hours. The mixture is now acidified with eight hundred (800) parts of hydrochloric acid of 20° Baumé and the coloring-matter precipitated by two hundred (200) parts of common salt. After stirring for about three

(3) days the coloring-matter is filtered off, pressed, and dried. The coloring-matter so obtained is a mixture consisting mainly of the product of the foregoing examples, but containing a brown substance of similar properties admixed. It can be used in dyeing without the isolation of its components one from the other, when a deeper black is obtained than in the absence of the brown product. If a larger percentage of 1.4' dinitronaphthalene be present, the shade becomes of a browner cast.

The mixed product possesses the properties of my new coloring-matter modified to a certain extent by the presence of the brown coloring-matter. It is a blue-black powder, easily soluble in cold water, giving a violet solution. It is not soluble in alcohol; but on boiling with anilin a brownish solution is obtained.

Now what I claim is—

1. As a new article of manufacture, the new violet-blue to blackish coloring-matter which can be derived from dinitronaphthalene and which is soluble in water, gives a blue color in ammoniacal water and which yields a fluorescent bluish or bluish-green color in concentrated sulfuric acid.

2. As a new article of manufacture, the new violet-blue to blackish coloring-matter, which can be derived from technical dinitronaphthalene and which is soluble in water, gives a blue color in ammonia-water and which yields a fluorescent bluish to bluish-green color in concentrated sulfuric acid and contains admixed a browner coloring-matter and so gives to boiling anilin a brown color, all substantially as described.

3. The process for the manufacture of a violet-blue to blue-black wool dyestuff by submitting a dinitronaphthalene to the action of a reducing agent, such as specified, in the presence of a sulfite in alkaline solution, all substantially as described.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

RENÉ BOHN.

Witnesses:

GUSTAV L. LICHTENBERGER,
BERNHARD C. HESSE.