UNITED STATES PATENT OFFICE.

JOHANN BAMMANN AND MORITZ ULRICH, OF ELBERFELD, GERMANY, ASSIGNORS TO THE FARBENFABRIKEN, VORMALS FR. BAYER & CO., OF SAME PLACE.

BLUE TETRAZO DYE.

SPECIFICATION forming part of Letters Patent No. 499,198, dated June 13, 1893.

Application filed January 19, 1893. Serial No. 458,992. (Specimens.) Patented in England August 26, 1890, No. 13,443; in Austria-Hungary November 28, 1890, No. 35,494 and No. 58,417; in France December 6, 1890, No. 210,033, and in Italy April 27, 1891, XXV, 29,631, LVIII, 100.

To all whom it may concern:

Be it known that we, JOHANN BAMMANN and MORITZ ULRICH, doctors of philosophy, chemists, and assignors to the FARBENFABRIKEN, VORMALS FR. BAYER & CO., of Elberfeld, subjects of the Emperor of Germany, residing at Elberfeld, Germany, have invented a new and useful Improvement in the Manufacture of Blue Coloring-Matters, (for which the aforesaid FARBENFABRIKEN has already obtained Letters Patent in the following countries: England, No. 13,443, dated August 26, 1890; France, No. 210,033, dated December 6, 1890; Italy, XXV, No. 29,631, and LVIII, No. 100, dated April 27, 1891; and Austria-Hungary, No. 35,494 and No. 58,417, dated November 28, 1890,) of which the following is a specification.

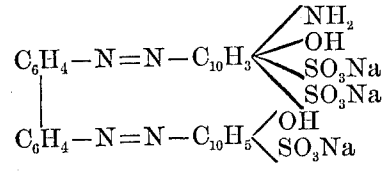
Our invention relates to the production of a new blue mixed tetrazo dye-stuff by combining in equimolecular proportions a tetrazo diphenyl salt either with amidonaphtholdisulpho acid and alphanaphtholalphamonosulpho acid or inversely at first with alphanaphtholalphamonosulpho acid and then with amidonaphtholdisulpho acid.

By amidonaphtholdisulpho acid we understand that alpha-amido alphanaphthol beta disulpho acid which we have described in a separate specification No. 432,495 and which was first produced by melting with caustic alkalies most practically at a temperature from about 180° to 190° centigrade the alphanaphthylamine trisulpho acid which is derived from the naphthalene trisulpho acid of Gürke and Rudolph and was first prepared by Koch by nitrating the said naphthalene trisulpho acid and reducing the alphamononitronaphthalene trisulpho acid thus formed. This amidonaphtholdisulpho acid, usually termed 1:8— amidonaphthol beta disulpho acid, is identical with the amidonaphtholdisulpho acid H which has been obtained afterward viz. by converting naphthalene 2:7— disulpho acid into its dinitro compound, reducing the latter and heating the diamidonaphthalene alpha disulpho acid thus formed with diluted acids as mentioned in the specification forming part of Letters Patent to Meinhard Hoffmann, No. 464,135, dated December 1, 1891.

In carrying out our process practically we proceed as follows: 1.84 kilos, by weight, of benzidine or the corresponding quantity of one of its salts are converted in hydrochloric solution by means of 1.4 kilos, by weight, of sodium nitrite into tetrazodiphenylchlorid. A solution in water of 3.63 kilos, by weight, of the sodium salt of the 1:8— amidonaphthol-beta disulpho acid hereinbefore specified is then allowed to flow into the above solution of tetrazodiphenyl chlorid. The resulting solution is rendered and kept moderately alkaline by the addition of sodium carbonate or the like or rendered weakly acid by means of acetic acid. After some hours the formation of the intermediate product is complete. The latter, after having been perfectly separated by adding common salt, is filtered off and introduced into a watery solution of 2.46 kilos, by weight, of the sodium salt of alphanaphtholalphamonosulpho acid (1:4) taking care by adding, for instance, sodium carbonate, that the solution remains alkaline during the whole operation. Of course, it is not necessary to filter off the first formed intermediate product, but the above moderately alkaline or acid solution containing the intermediate product resulting from one molecular proportion of tetrazo diphenyl and amidonaphthol disulpho acid can be added directly to the alkaline solution of the sodium salt of the alphanaphthol alpha monosulpho acid (1:4), taking care that the liquid remains alkaline. After about twelve hours the mixture is heated for a short time at about 60° centigrade, in order to complete the reaction, and the complete dye-stuff is isolated in the usual manner by salting out, filtering off, pressing and drying. The same coloring-matter results, if in analogous manner one molecular proportion of tetrazodiphenyl salt is first coupled with one molecular proportion of alphanaphtholalphamonosulpho acid (1:4) in alkaline or acetic solution to form a so called intermediate product and if the latter subsequently is combined with one molec-

ular proportion of the aforesaid 1:8—amidonaphthol beta disulpho acid, the latter operation being effected most practically in moderately alkaline solution. Of course, in place of the sodium salts of amidonaphthol disulpho acid and alphanaphtholalphamonosulpho acid, the corresponding quantities of other alkaline salts of these two acids or the corresponding quantities of these two acids in the free state can be employed.

Our new coloring-matter having the formula:



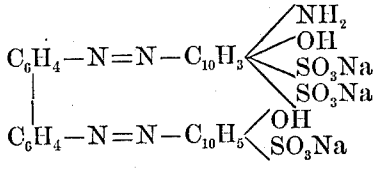
forms after drying and pulverizing a grayish-black powder soluble in water with bluish-red (ruby-red) color, which is somewhat more reddish, than is the color, with which the analogous product obtained from tolidine dissolves in water. It is somewhat soluble in alcohol with bluish-red color and dissolves with the same color in ammonia and soda-lye. By sodium carbonate it is dissolved with bluish-red color, especially on heating. In diluted hydrochloric or sulphuric acid it is insoluble. When its watery solutions are mixed with ammonia, the color becomes somewhat more bluish, and after some time bluish-violet flakes are separated, while by an addition of sodium carbonate the color is rendered at first a little redder and thereupon the liquid gradually becomes dull. On adding soda-lye to its watery solutions the color becomes a little clearer, while an excess of soda-lye renders the liquid dull and slowly effects the separation of dark bluish-red flakes. If diluted hydrochloric or sulphuric acid is added to its solution in water, the liquid first becomes bluer and clearer, then dark bluish-red or brownish-red flakes are gradually separated after some time. It dissolves in concentrated sulphuric acid with greenish-blue color, which turns into reddish-violet on adding ice water; at last reddish-blue flakes are separated. On unmordanted cotton it produces blue shades. When the fiber dyed with our new product is treated in a moderately acidulated solution of sodium nitrate and subsequently in a weakly alkaline solution of betanaphthol, from gray to black shades result.

Our new dye-stuff differs by its composition from the three coloring-matters which we have described in three separate specifications, Serial Nos. 458,993, 458,991 and 459,086, and of which the one results by the combination of tetrazo orthoditolyl salt, 1:8—amidonaphtholbetadisulpho acid and alphanaphtholal phamonosulpho acid, while the other is obtained by combining equimolecular proportions of tetrazo orthoditolyl salt, 1:8— amidonaphthol beta disulpho acid and 2:6— dihydroxynaphtholene and the third is obtained from equimolecular proportions of a tetrazodiphenyl salt, amidonaphtholdisulpho acid and alphanaphthylamine. It likewise differs by its composition from the two products described by us in the applications filed December 18, 1891, Serial Nos. 415,515 and 415,516 and obtained from one molecular proportion of benzadine or tolidine and two molecular proportions of 1:8— amidonaphtholbeta disulpho acid.

Having thus described the nature of this invention and in what manner the same is to be carried out, that which we claim as new, and desire to secure by Letters Patent, is—

1. The process of producing a new blue coloring matter by combining equimolecular proportions of a tetrazodiphenyl salt, with 1:8—amidonaphthol beta disulpho acid and alpha-naphthol alphamonosulpho acid by preference in alkaline solution or equivalent process.

2. As a new product the coloring-matter having the formula:



dyeing unmordanted cotton blue shades; forming a grayish black powder soluble in ammonia, soda lye and sodium carbonate with bluish red color; slightly soluble in alcohol with bluish red color, insoluble in dilute hydrochloric or sulfuric acid. Soluble in concentrated sulfuric acid with greenish blue color changing to a reddish violet on addition of ice water, from which solution, finally, reddish blue flakes separate; soluble in water with a ruby red color, which solution turns slightly bluer, on addition of ammonia, and separates after some time, bluish violet flakes, while, on addition of sodium carbonate the aqueous solution turns slightly redder and gradually becomes dull, and, on addition of soda lye, the aqueous solution becomes slightly clearer, but grows dull and separates a dark bluish red precipitate, when an excess of soda lye is added, and having the qualities substantially as specified.

In testimony whereof we have signed our names in the presence of two subscribing witnesses.

JOHANN BAMMANN.
MORITZ ULRICH.

Witnesses:
WM. ESSENWEIN,
RUDOLPH FRICKE.

Correction in Letters Patent No. 499,198.

It is hereby certified that in Letters Patent No. 499,198, granted June 13, 1893, upon the application of Johann Bammann and Moritz Ulrich, of Elberfield, Germany, for an improvement in "Blue Tetrazo Dyes," an error appears in the printed specification requiring the following correction, viz.: In line 53, page 2, the word "nitrate" should read *nitrite;* and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed, countersigned, and sealed this 27th day of June, A. D. 1893.

[SEAL]

JNO. M. REYNOLDS,
Assistant Secretary of the Interior.

Countersigned:

S. T. FISHER,
Acting Commissioner of Patents.