UNITED STATES PATENT OFFICE.

ARMAND JULIUS STIEGELMANN, OF LUDWIGSHAFEN, GERMANY, ASSIGNOR TO BADISCHE ANILIN & SODA FABRIK, OF SAME PLACE.

PROCESS OF MAKING INDIGO FROM INDIGO-LEUCO COMPOUNDS.

SPECIFICATION forming part of Letters Patent No. 680,894, dated August 20, 1901.

Application filed May 21, 1901. Serial No. 61,275. (No specimens.)

To all whom it may concern:

Be it known that I, ARMAND JULIUS STIEGELMANN, doctor of philosophy and chemist, a subject of the Emperor of Germany, residing at Ludwigshafen-on-the-Rhine, in the Kingdom of Bavaria, Germany, have invented new and useful Improvements in Processes for the Production of Indigo from Indigo-Leuco Compounds, of which the following is a specification.

I have found that sulfur enters readily into reaction with indigo-leuco compounds, such as indoxyl, indoxylic acid, and indigo-white. The reaction consists, apparently, in a combination of the sulfur with hydrogen of the leuco compounds whereby sulfureted hydrogen is formed. In any case the indigo-leuco compound is converted into indigo. The said reaction can be effected in the presence or in the absence of textile fiber. If textile material suitably prepared with sulfur be introduced into an indigo-vat, the conversion of the indigo-white to indigo-blue takes place at once in the vat during the dyeing process. Animal and vegetable fiber have the property of fixing sulfur mechanically. If material that has been suitably prepared with sulfur be dyed in an indigo-vat, the presence of the sulfur causes the indigo to be taken up by the fiber essentially faster than if no sulfur be present, and the formation of indigo takes place already within the vat. Thus woolen material suitably prepared with sulfur upon dyeing in the indigo-vat in a short time and while immersed in the vat assumes an indigo-blue color, and in one passage through the vat it is dyed approximately as strongly and as fast as unprepared wool would be dyed by three passages through the same vat.

My new process of dyeing can be carried out by using an indigo-vat that is kept alkaline by means of lime, magnesia, or other alkaline earth, and it is applicable to cotton and to woolen goods.

A special application of the new process of great technical importance consists in preparing or impregnating woolen or cotton material in some parts with sulfur while leaving the other parts free from sulfur. Upon dyeing such material in the vat the parts prepared with sulfur assume a darker shade than the others. In this way a pattern in light and dark blue can be prepared in a simple manner, while hitherto such effects could only be achieved by means of a complicated process.

My new process can only be advantageously applied when printing indigo shades. For instance when printing with indophor (indoxylic acid) the process prior to my invention consisted in printing this body onto the material and then passing the material through a bath containing an oxidizing agent, such as ferric chlorid. According to my present invention a mixture of indophor and sulfur is printed on the goods, and then upon steaming the indigo-blue is directly formed upon the fiber.

Instead of preparing material with sulfur itself mixtures producing sulfur, such as sulfid of sodium or sulfid of calcium, with acids, can be employed.

The following examples will serve to illustrate the manner in which my invention may best be carried into practical effect; but the invention is not confined to the reactions exemplified nor to the conditions described therein. The parts are by weight.

Example 1—Oxidation of indoxylic acid to indigo.—Prepare a melt rich in indoxylic acid in the manner described in the specification of English Letters Patent No. 9,291 of 1894. Dissolve about fifty (50) parts of the melt in water and add dilute sulfuric acid until the solution is but weakly alkaline or neutral. Then add four (4) parts of finely-divided sulfur while slowly warming the solution. The indigo separates out and can be collected in the usual way.

Example 2—Dyeing loose wool or other woolen material.—Dissolve one hundred and twenty (120) parts of sodium thiosulfate and five (5) parts of alum in three hundred (300) parts of water. To this add a solution of about five (5) parts of concentrated sulfuric acid, (containing about ninety-six per cent. of H_2SO_4.) In this way a suspension of finely-divided sulfur in water is obtained. Introduce about two hundred and fifty (250) parts of the material to be dyed into this bath at ordinary temperature. Manipulate the woolen material in the bath for about half ($\frac{1}{2}$) an

hour while raising the temperature to about fifty (50°) to fifty-five (55°) degrees centigrade. Press out the water, swill with cold water, and introduce the goods into the vat. The passage of the goods through the vat should occupy about half an hour, so that the effect of the sulfur may be thoroughly exercised.

Example 3—Production of a dark-blue pattern on light-blue ground on woolen material.—Print the material with a paste consisting of eighty (80) per cent. of gum-thickening (1:1) and twenty (20) per cent. of finely-divided sulfur, (flowers of sulfur.) After printing steam for about five (5) minutes with damp steam and pass the material into the vat. The parts prepared with sulfur assume a darker-blue shade than the unprinted parts assume.

Example 4—Production of a dark-blue pattern on light-blue ground on cotton, linen, or mixed cotton and linen goods.—Print the material with a mixture of eighty (80) parts of gum-thickening, (1:1,) four (4) parts of finely-divided sulfur, ten (10) parts of caustic-soda lye, (containing about thirty-five per cent. of NaOH.) After printing steam the goods with dry steam for about five (5) minutes, then pass the material through acidified water and swill lightly with cold water. Dye in a vat of medium strength, allowing the material to remain in the vat for about half ($\frac{1}{2}$) an hour.

Example 5—Indigo-printing with indophor.—Print the cotton material with a mixture of fifty (50) parts of indophor well mixed with twenty (20) parts of finely-divided sulfur, two hundred (200) parts of a solution of borax of three (3°) degrees Baumé, and seven hundred and thirty (730) parts of tragacanth thickening, (50:1,000.) Steam for five (5) minutes and swill with water.

Now what I claim is—

1. The process for the production of indigo from an indigo-leuco compound by causing the latter to react with sulfur, substantially as described.

2. The process for the production of indigo from an indigo-leuco compound by causing the latter to react with sulfur in the presence of textile material, substantially as described.

3. The process for the production of indigo from an indigo-leuco compound in the presence of textile material by impregnating the textile material with sulfur and causing the sulfur to react with an indigo-leuco compound, substantially as described.

4. The process for the production of indigo from an indigo-leuco compound in the presence of textile material which consists in impregnating part of the said textile material with sulfur and causing the said sulfur to react with an indigo-leuco compound, substantially as described.

5. The process for the production of indigo from an indigo-leuco compound in the presence of textile material which consists in printing the textile material with a mixture of an indigo-leuco compound and sulfur and causing the sulfur to react with the indigo-leuco compound, substantially as described.

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

ARMAND JULIUS STIEGELMANN.

Witnesses:
HENRY HASPER,
WOLDEMAR HAUPT.