

UNITED STATES PATENT OFFICE.

RUDOLPH KNIETSCH AND PAUL SEIDEL, OF LUDWIGSHAFEN, GERMANY, AS-
SIGNORS TO THE BADISCHE ANILIN AND SODA FABRIK, OF SAME PLACE.

INDOXYLIC ACID AND PROCESS OF MAKING IT.

SPECIFICATION forming part of Letters Patent No. 546,165, dated September 10, 1895.

Application filed May 17, 1895. Serial No. 549,709. (No specimens.) Patented in France November 12, 1894, No. 206,982; in Belgium November 17, 1894, No. 112,744; in Italy December 6, 1894, XXIX, 37,665, and LXXIII, 498, and in Austria December 24, 1894, No. 44/6,512.

To all whom it may concern:

Be it known that we, RUDOLPH KNIETSCH, doctor of philosophy, a subject of the King of Prussia, German Emperor, and PAUL SEIDEL, doctor of philosophy, a subject of the King of Saxony, residing at Ludwigshafen-on-the-Rhine, in the Kingdom of Bavaria and Empire of Germany, have invented new and useful Improvements in the Manufacture of a New Indoxyllic Acid, (for which patents have been obtained in France, No. 206,982, (certificat d'addition,) dated November 12, 1894; in Austria, 44/6,512, dated December 24, 1894; in Belgium, No. 112,744, dated November 17, 1894, and in Italy, XXIX, 37,665, LXXIII, 498, dated December 6, 1894,) of which the following is a specification.

Our invention relates to the manufacture of a new commercial product suited for use in printing indigo-blue shades on textile fabrics. In the Letters Patent No. 534,560, granted to Karl Heumann, there is described the production of a new artificial indigo-white from phenyl-glycocoll-ortho-carboxylic acid by treating with alkali. This is described as consisting of an intimate combination or mixture of unaltered alkali or alkaline earth with a body having the nature of a leuco compound and with other products of the reaction. We have found that the nature of this contained leuco body varies according to the conditions under which the reaction is effected, and that usually the leuco body is a mixture of indoxyl and an indoxyllic acid in the form of alkaline salt. We have discovered modifications of the process for treating the phenyl-glycocoll-ortho-carboxylic acid with alkalies whereby it is possible with certainty to produce an artificial indigo-white containing indoxyllic acid only, to the practical exclusion of indoxyl. This is effected by the use of caustic soda in the treatment of the phenyl-glycocoll-ortho-carboxylic acid and at a temperature rising to about 240° to 265° centigrade. From this artificial indigo-white we prepare and isolate our new indoxyllic acid. This is effected by dissolving the artificial indigo-

white in ice-water and precipitating the indoxyllic acid by the addition of sulfuric or hydrochloric acid or a stronger organic acid. Indoxyllic acid, as heretofore obtained by the process of Baeyer, and as described in the text-books, contains more or less combined haloid elements, as bromin or chlorin; but indoxyllic acid as obtained by our process is entirely free from haloid elements.

The following example will serve to illustrate the manner in which our invention can best be carried into practical effect. The parts are by weight.

Example: Mix about ten (10) parts of sodium phenyl-glycocoll-ortho-carboxylate, which must be quite neutral and thoroughly dried with about twenty (20) parts of caustic soda, which must also be as free from water as possible. Grind these two ingredients together, so that they become thoroughly mixed, and spread the fine powder so obtained in a thin layer. Then heat uniformly to a temperature of about two hundred and forty to two hundred and sixty-five degrees centigrade, (240°-265°C.) Throughout the operation the atmospheric air must be excluded as far as conveniently possible. This can be done, for example, by conducting the operation in an atmosphere of an indifferent gas, such as nitrogen, hydrogen, or the like. As the mass does not melt, the period of heating depends upon the thickness of the layer. In general, from half an hour to one hour's heating after the temperature mentioned is attained, is requisite. Allow the mass to cool. It should then possess a uniform lemon-yellow color throughout. The presence of a whitish mass in the interior indicates that the reaction is not complete and the heat must be maintained longer. Next grind about fifty (50) parts of the artificial indigo-white so obtained to powder and add it to a mixture of about four hundred (400) parts of ice and about one hundred and seventy-five (175) parts of dilute sulfuric acid containing about twenty-two per cent. (22%) real acid (H_2SO_4). The indoxyllic acid separates out as a pre-

5 cipitate. Filter and wash with ice-cold water. In the moist state the acid is unstable, but becomes more stable after drying. Drying must be effected at a moderate heat (not above 50° centigrade) by spreading the material over a large surface. It is advantageous, but not necessary, to exclude the oxygen of the atmosphere.

10 Our new commercial product is a gray powder but slightly soluble in cold water, soluble in alcohol and ether. It is readily soluble in alkaline water, and the solution turns blue from formation of indigotin on exposure to the action of the atmospheric oxygen.

15 This new product differs from the substance heretofore known as "indoxylic acid," and described as such, in the fact that it is completely free from combined halogen, as can be seen by oxidizing to indigotin in alkaline solution, filtering off the indigotin, washing and testing the indigotin for halogens in the usual way—for instance, by treating with caustic lime, dissolving in nitric acid and testing for the haloid elements by means of nitrate of silver. The old indoxylic acid described in literature has existed solely as a scientific curiosity, and from its costliness and difficulty of production could never be commercially manufactured.

Now, what we claim is—

30 1. As a new product the indoxylic acid which can be produced by the reaction of phenyl-glycocol-ortho-carboxylic acid with caustic soda, and which is a gray powder but slightly soluble in cold water, soluble in alcohol and ether, soluble in alkaline water, being readily oxidizable in alkaline solution to indigotin and which is entirely free from combined halogen and on heating gives off carbonic acid gas, all substantially as described.

40 2. The herein described process of producing a new indoxylic acid which consists in treating phenyl-glycocol-ortho-carboxylic acid with caustic soda at about 240° to 265° centigrade, then treating the melt with ice cold dilute acid, then filtering and washing the precipitate, substantially as described.

45 In testimony whereof we have hereunto set our hands in the presence of two subscribing witnesses.

RUDOLPH KNIETSCH.
PAUL SEIDEL.

Witnesses:

ERNEST F. EHRHARDT.
ADOLPH RENTLINGER.