

UNITED STATES PATENT OFFICE.

BRUNO RICHARD SEIFERT, OF RADEBEUL, AND CURT PHILIPP AND MAX HERMANN GMEINER, OF DRESDEN, GERMANY, ASSIGNORS TO CHEMISCHE FABRIK VON HEYDEN, ACTIENGESSELLSCHAFT, OF RADEBEUL, NEAR DRESDEN, GERMANY.

PROCESS OF MAKING INDIGO AND INTERMEDIATE PRODUCTS.

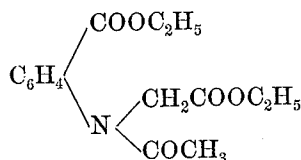
SPECIFICATION forming part of Letters Patent No. 714,042, dated November 18, 1902.

Application filed December 21, 1901. Serial No. 86,796. (Specimens.)

To all whom it may concern:

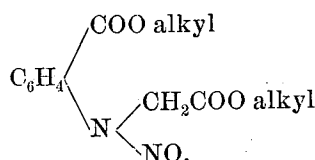
Be it known that we, BRUNO RICHARD SEIFERT, a resident of Radebeul, near Dresden, and CURT PHILIPP and MAX HERMANN GMEINER, residents of Dresden, Kingdom of Saxony, Germany, subjects of the King of Saxony, have invented a new and useful improvement in Processes of Making Indigo and Intermediate Products, of which the following is a specification.

Vorlaender and Weissbrenner (*Bericht der Deutschen Chemischen Gesellschaft* 33, page 556) have observed that the acetyl-phenyl-glycin-o-carboxylic acid diethyl ester



is transformed into indoxyl and indigo by the action of twenty per cent. boiling potash-lye. The Badische Anilin und Soda Fabrik has carried the research in this direction further and extended this reaction to the neutral esters of phenyl-glycin-o-carboxylic acid, which are substituted in the nitrogen by an organic acid residue. (French Patent No. 295,814.) We have now discovered that these expensive organic acid residues can be replaced with good results by a very cheap inorganic acid residue—namely, the nitroso group. These hitherto unknown alkyl esters of nitroso-phenyl-glycin-o-carboxylic acid are obtained in quantitative yield by the action of nitrosifying agents upon the dialkyl esters. For example, two hundred and fifty-one parts phenyl-glycin-o-carboxylic acid diethyl ester are dissolved in one thousand parts glacial acetic acid and into the mixture, cooled to 0° centigrade, there is allowed to run, while well stirring, a solution of seventy to seventy-two parts sodium nitrite in two hundred parts water. The mixture is then poured onto ice-water, when the nitroso diester separates out as heavy dark-red oil. The nitrosification of the dialkyl esters can naturally also be effected according to the other usual methods of nitrosi-

fying. In the same way nitrosified dialkyl esters of phenyl-glycin-ortho-carboxylic acids, in which nucleus hydrogen is substituted by substitutes, are obtained by nitrosifying the dialkyl esters of those substituted acids. These nitrosified dialkyl esters are oily bodies of the constitution



They are transformed with striking ease into indoxyl derivatives and indigo on treatment with solutions having an alkaline reaction.

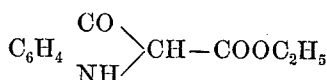
Example I: One part nitroso-phenyl-glycin-o-carboxylic acid diethyl ester is heated to boiling, with ten parts twenty-per-cent. potash-lye, using a reflux condenser and care being taken to exclude the air as far as possible. After the ester is completely dissolved the contents of the boiler are cooled and air is led through them, when the indigo coloring-matter separates out. Indigo coloring-matters substituted in the nucleus are obtained by the employment of nitrosified phenyl-glycin-o-carboxylic acid esters substituted in the nucleus. The treatment of the nitroso esters may with advantage be carried out with agents having an alkaline reaction in the presence of reducing agents. Thus substances having an alkaline and reducing action—for example, alkaline sulfids—are particularly suitable for the purpose.

Example II: One hundred parts, by weight, of the nitroso-phenyl-glycin-o-carboxylic acid diethyl ester are mixed into nine hundred parts of a ten-per-cent. aqueous solution of sodium sulfid and while being well stirred are heated on the water-bath until a pretty brisk reaction begins. After the completion of same one hundred and eighty parts of a thirty-four-per-cent. soda-lye are allowed to run in and the mixture is heated for several hours on the water-bath until the formation of the indigo leuco compound or "vat" is completed. Dilution is then made with one

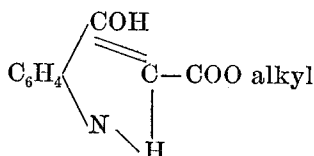
thousand parts water, and the indigo is precipitated by leading in a current of air. The indigo is filtered off, washed, and dried.

Instead of first treating with alkali sulfid and then with soda-lye alkali sulfid can be used alone, and in general substances which have a simultaneous alkaline and reducing action can be used.

The formation of the indigo coloring-matters from the nitroso esters, as hereinbefore described, takes place in two or three phases of reaction, which, if desired, can be kept separate. In the first phase the nitroso esters are transformed into ammonia insoluble intermediate products, most likely pseudo-indoxylic acid esters

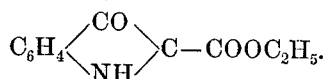


which in the second phase are transformed by the further treatment with alkaline agents into indoxylic acid esters



which are soluble in ammonia and which in the third phase are transformed by the further treatment with alkali into indoxyl or indigo leuco compound or vat. This third phase is already known in literature. If it is desired to stop the reaction at the end of the first phase, the procedure may be, for example, as follows:

Example III: Two hundred and eighty parts, by weight, of nitroso-phenyl-glycin-o-carboxylic acid diethyl ester are dissolved in one thousand parts of alcohol, two hundred and fifty parts, by weight, of a thirty-per-cent. ammonia are added and sixty-eight to seventy parts of sulfureted hydrogen are introduced while well cooled. After standing for several days at the ordinary temperature the precipitated sulfur is filtered off and the alcohol is completely distilled off. The residue is treated with diluted aqueous ammonia for separating out the indoxyl acid ester formed and finally recrystallized from alcohol with the aid of bone-black. In this way yellow-green crystals of fusing-point 183° centigrade are obtained. These are insoluble in water and alkalis, hardly soluble in alcohol, more readily soluble in glacial acetic acid. According to its action and to analysis the compound seems to be the pseudo-indoxylic acid ester isomeric to the indoxylic acid ester soluble in alkali, which pseudo ester is of the constitution



This compound is in further treating it with

substances acting in an alkaline manner transformed without difficulty into the normal alkali soluble indoxylic acid ester. (By treating with acids the compound remains essentially unchanged.) If it is desired to stop the reaction at the end of the second phase, the procedure may be, for example, as follows:

Example IV: One hundred parts nitroso-phenyl-glycin-o-carboxylic acid diethyl ester are stirred into six hundred parts of a twenty-per-cent. soda-lye at ordinary temperature. After a short time the separation of crystals of the sodium compound of the indoxylic acid ethyl ester begins, and after twelve to fourteen hours the reaction mass sets to a thick paste. This is siphoned or drawn off, dissolved in water, and acidified. The compound thus precipitated shows itself to be identical in all respects with the indoxylic acid ethyl ester first prepared by A. von Baeyer.

Instead of using agents having only an alkaline reaction for the first phase agents having an alkaline and reducing action can also be used with advantage.

Example V: One hundred parts nitroso-phenyl-glycin-o-carboxylic acid diethyl ester are heated on the water-bath with a solution of seventy parts of sodium sulfid in one thousand parts water until a pretty violent reaction commences, being well stirred during heating. After the termination of the reaction the mixture is allowed to cool, supersaturated with dilute acid, and filtered. From the residue of filtration the indoxylic acid ester can be extracted by the usual extracting media—for example, alcohol, ether, &c.

The indoxylic acid esters, as is already known in literature, are transformed into indigo by further heating with alkali and oxidation of the resulting leuco compound or vat by air or other oxidizing agents.

We claim—

1. The herein-described improvement in the process of producing indigo coloring-matters consisting in transforming the dialkyl esters of nucleus-substituted and non-substituted phenyl-glycin-o-carboxylic acids into the products nitrosified in the nitrogen, treating the same with agents having an alkaline reaction and oxidizing the leuco compound or "vat" thus obtained.

2. The herein-described improvement in the process of producing indigo coloring-matters consisting in transforming the dialkyl esters of nucleus-substituted and non-substituted phenyl-glycin-o-carboxylic acids into the products nitrosified in the nitrogen, treating the same with agents having an alkaline and reducing action and oxidizing the leuco compound or "vat" thus obtained.

3. The herein-described improvement in the process of producing indigo coloring-matters consisting in transforming the dialkyl esters of nucleus-substituted and non-substi-

tuted phenyl-glycin-o-carboxylic acids into the products nitrosified in the nitrogen by treating these esters with nitrosifying agents, converting these nitrosified esters into pseudo-indoxylic acid esters, transforming the latter into indoxylic acid esters and transforming those indoxylic acid esters into indigo coloring-matters by further action of alkalies and oxidation.

10 4. The herein-described method of producing the intermediate product pseudo-indoxylic ester consisting in treating the nitrosified esters of phenyl-glycin-o-carboxylic acids with agents having an alkaline action.

15 5. The herein-described method of producing the intermediate product pseudo-indoxylic ester consisting in treating the nitrosified esters of phenyl-glycin-o-carboxylic acids with agents having an alkaline action, in the presence of reducing agents.

20 6. The pseudo-indoxylic acid ester herein described, as a new technical body which is a crystalline powder insoluble in water and al-

kalies and capable of being transformed by alkaline agents into indoxylic acid ester. 25

7. The herein-described method of producing the intermediate product indoxylic acid ester consisting in treating the nitrosified esters of phenyl-glycin-o-carboxylic acids with agents having an alkaline action. 30

8. The herein-described method of producing the intermediate product indoxylic acid ester consisting in treating the nitrosified esters of phenyl-glycin-o-carboxylic acids with agents having an alkaline action, in the presence of reducing agents. 35

In testimony that we claim the foregoing as our invention we have signed our names, in presence of two witnesses, this 9th day of December, 1901.

BRUNO RICHARD SEIFERT.

CURT PHILIPP.

MAX HERMANN GMEINER.

Witnesses:

HERNANDO DE SOTO,

PAUL ARRAS.