UNITED STATES PATENT OFFICE.

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PROCESS FOR PREPARING INDOXYLS AND INDIGO COLORING-MATTERS.

984,442. Specification of Letters Patent. Patented Feb. 14, 1911.

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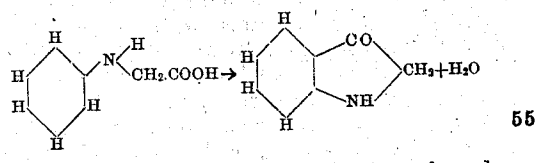
To all whom it may concern:

Be it known that I, ARNOLD RAHTJEN, a subject of the German Emperor, and resident of Hamburg, Germany, have invented certain new and useful Improvements in Processes of Preparing Indoxyls and Indigo Coloring-Matters, of which the following is a specification.

It is a well known fact that substances which contain the group $NHCH_2CO$ one or more times in the molecule may be converted by melting with alkali hydroxids into indoxyls from which indigo may be prepared in the well known manner. However, the yields obtained by this process, as, for instance, when phenylglycin (anilido-acetic acid) is used, are so small that the process must be considered as a commercially impracticable one which cannot be employed for the manufacture of indigo on a large scale. It has been now found that an excellent yield of indoxyls and, consequently, of indigo may be obtained by electrolyzing substances of the aromatic or cyclic type and containing an aryl group linked to one or more groups of the general type $(NR.CH_2.CO)$, in which R represents hydrogen or an organic radical, in admixture with bodies capable of yielding metal ions upon electrolysis, such as the alkali hydrates, singly or admixed, oxids or hydrates of alkaline earths, or electrolyzable salts of alkalis or alkaline earths capable of yielding metal ions. Substances which serve as fluxes or diluting agents may be employed, advantageously. Electrolysis may be carried out with or without the employment of a diaphragm. The experiments made to date have given yields up to and beyond 70% (seventy per cent.) of the theory.

In general it may be stated that substances of the aryl-glycin type are suitable for employment in this process, including under this generic term the aryl-glycins *per se* and their homologues, esters and salts, as well as their acetyl and other derivatives. When phenylglycin ($C_6H_5.NH.CH_2COOH$) is employed, the reaction which occurs is sometimes written as follows:



water being eliminated from the phenylglycin with formation of indoxyl. Equations such as this must be taken, however, as purely theoretical and as merely indicative of probable reactions, rather than as representing ascertained facts. This result could not have been anticipated, for it might have been expected that the organic bodies employed, such as salts of phenylglycin, etc., would be entirely decomposed by the electric current. Such is not the case, but with sensitive substances it is often useful to employ a diaphragm whereby the hydroxyl ions, which are prejudicial, may be conveyed in the simplest possible manner into the anode chamber and thus rendered harmless.

The favorable result of employing the electric current appears to reside in the fact that the alkaline metal is enabled to react *in statu nascendi;* and in a state of fine division that cannot be obtained by mechanical means.

The temperature of the materials, and the tension and the density of the current employed may vary between large limits. Good outputs are obtained when the electrolysis is carried on at a temperature between 160—300 degrees C. and with 1 to 10 volts and 0.2 to 20 amperes per square decimeter of surface of electrodes.

Typical substances which may be employed are, phenylglycin-phenylglycin and phenylhydantoin as well as their homologues, salts, ethers, etc., and their acetyl and other derivatives. The electrodes and diaphragms employed may be those usually utilized for electrolyzing alkali hydroxids.

In a typical example of my invention, 100 parts of a molecular mixture of sodium and potassium hydroxids are mixed with 30 parts of acetylphenylglycin-o-carbonate of potassium and the mixture heated to about 220 to 260 degrees C. and fused in the cathode chamber of a suitable electrolytic cell. The anode chamber may be charged with the same molecular mixture of the alkali hydroxids alone. The mixture in each chamber may contain alkaline earths or salts and alkalis or alkaline earths or diluting fluxes. The cell may serve as a cathode and carbon be employed as an anode. The electrolysis may be advantageously carried out with a current of about 4 to 6 volts and about 2 to 5 amperes per square decimeter, the liquid mass being well stirred. The operation is continued until for each molecule of substance a little more than one atom of alkali metal has been set free, which may easily be calculated with the aid of the given data. After cooling down the molten mass, it may be introduced into water and the indigo coloring matters prepared in the well known manner. The output with this mode of operating, as shown by experiments that have been made, is about 70 per cent. of the theory.

Suitable precautions may be taken during the electrolysis to obviate or remove by-products of the reaction, such as free alkali metal and water.

During the electrolysis, suitable reactive gases or vapors such as ammonia or hydrazin may be conveyed through or over the mass in order to convert liberated sodium etc., set free in molecular form, into the corresponding metal amids or metal imids. The reaction may be carried out under reduced pressure or vacuum and I preferably carry out the electrolysis in a vigorous or lively manner at the beginning, and during the period of formation of water so that the water formed is at once rendered harmless.

Having now fully described my said invention, what I claim and desire to secure by Letters Patent, is—

1. A process of preparing indoxyls and indigo coloring bodies which comprises electrolyzing a mass comprising alkali hydroxids and a substance of the aryl-glycin type, and treating the resulting mass to recover indoxyl and indigo therefrom.

2. A process of preparing indoxyls and indigo coloring bodies which comprises electrolyzing a mass comprising alkali hydroxids and other electrolyzable inorganic substances and a substance of the aryl-glycin type and treating the resulting mass obtained to recover indoxyl and indigo therefrom.

3. A process of preparing indoxyls and indigo coloring bodies which comprises electrolyzing a mass comprising alkali hydroxids and diluting agents and a substance of the aryl-glycin type and treating the resulting mass obtained to recover indoxyl and indigo therefrom.

4. A process of preparing indoxyls and indigo coloring bodies which comprises electrolyzing a mass comprising alkali hydroxids mixed with fluxes and a substance of the aryl-glycin type and treating the resulting mass to recover indoxyl and indigo therefrom.

5. A process of preparing indoxyls and indigo coloring bodies which comprises electrolyzing a mass comprising alkali hydroxids and other electrolyzable inorganic substances and diluting agents and a substance of the aryl-glycin type and treating the resulting mass obtained to recover indoxyl and indigo therefrom.

6. A process of preparing indoxyls and indigo coloring bodies which comprises electrolyzing a mass comprising alkali hydroxids and other electrolyzable inorganic substances and fluxes and a substance of the aryl-glycin type and treating the resulting mass obtained to recover indoxyl and indigo therefrom.

7. A process of preparing indoxyls and indigo coloring bodies which comprises electrolyzing a mass comprising an alkali hydroxid and a substance of the aryl-glycin type and during such electrolysis removing by-products of the reaction, and treating the resulting mass obtained to recover indoxyl and indigo therefrom.

8. A process of preparing indoxyls and indigo coloring bodies which comprises electrolyzing a mass comprising an alkali hydroxid and other substances capable of evolving metal ions, a fluxing body, a diluting body and a substance of the aryl-glycin type, and treating the resulting mass obtained to recover indoxyl and indigo therefrom.

9. A process of preparing indoxyls and indigo coloring bodies which comprises electrolyzing a mass comprising alkali hydroxids and a substance of the aryl-glycin type and during such electrolysis contacting a reactive gas with such mass to prevent formation of free metal, and treating the resulating mass obtained to recover indoxyl and indigo therefrom.

10. A process of preparing indoxyl and indigo coloring bodies which comprises electrolyzing a mass comprising alkali hydroxids and a substance of the aryl-glycin type, the electrolysis being carried on with an increased current during the formation of water so that the water formed is at once rendered harmless, and treating the result-

ing mass obtained to recover indoxyl and indigo therefrom.

11. A process of preparing indoxyls and indigo coloring bodies, which comprises electrolyzing a mass comprising alkali hydroxids and a substance in which an aryl group is linked to the group —NR—CH_2—CO—, and treating the resulting mass to produce indigo coloring bodies.

12. A process of preparing indoxyls and indigo coloring bodies, which comprises electrolyzing a mass comprising alkali hydroxids and a substance in which a phenyl group is linked to the group —NR—CH_2—CO—, and treating the resulting mass to produce indigo coloring bodies.

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

ARNOLD RAHTJEN.

Witnesses:

ERNEST H. L. MUMMENHOFF,

IDA CHRIST. HAFERMANN.