

UNITED STATES PATENT OFFICE.

PAUL JULIUS, VIKTOR VILLIGER, AND PAUL NAWIASKY, OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY, ASSIGNORS TO BADISCHE ANILIN & SODA FABRIK, OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY, A CORPORATION OF GERMANY.

DICHLOR-DIBROM-INDIGO AND PROCESS OF MAKING SAME.

957,683.

Specification of Letters Patent.

Patented May 10, 1910.

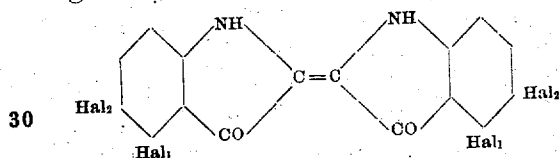
No Drawing.

Application filed November 17, 1909. Serial No. 528,563.

To all whom it may concern:

Be it known that we, PAUL JULIUS, Ph. D., VIKTOR VILLIGER, Ph. D., and PAUL NAWIASKY, Ph. D., chemists, subjects the first and third of the Emperor of Austria, the second, a citizen of the Swiss Republic, residing at Ludwigshafen-on-the-Rhine, Germany, have invented new and useful Improvements in Dichlor-Dibrom-Indigo and Processes of Making Same, of which the following is a specification.

Our invention relates to the production of dichlor-dibrom-indigo in which the four halogen atoms are in the positions 4.4'.5.5'. We have invented a process for the production of our dichlor-dibrom-indigo by the saponification and oxidation of an ester of the corresponding chlor-brom-indoxyl carboxylic acid. Thus, upon operating in this way upon the methyl ester of 4.5-chlor-brom-indoxyl carboxylic acid, or of 4.5-brom-chlor-indoxyl carboxylic acid, we obtain the new product symmetrical 4.4'.5.5'-dichlor-dibrom-indigo, of a constitution corresponding to the formula



in which Hal₁ and Hal₂ are, the one, chlorine, and, the other, bromine. It consists when dry of a greenish blue powder which yields a blue solution in cold concentrated sulfuric acid and a blue solution in hot dimethyl anilin. It differs from all known dichlor-dibrom-indigos in that it dyes cotton from a vat exceptionally greenish shades of blue, which are fast against the action of washing, light, and chlorine. Moreover, the said shades when viewed by artificial light retain their greenish tint, whereas the other tetra-halogen indigos hitherto described assume a reddish or violet-black tint under similar circumstances.

The following example will serve to illustrate further the nature of this invention and how it can be carried into practical effect, but our invention is not confined to this example. The parts are by weight. In this example, we first, for the sake of convenience, describe the production of the methyl ester of chlor-brom-indoxyl carboxylic acid used in carrying out the process of the example. Introduce, while stirring, three hundred and thirty-seven parts of the methyl ester of 3.4-chlor-brom-phenyl-glycin-2-carboxylic acid, or of 3.4-brom-chlor-phenyl-glycin-2-carboxylic acid into a solution of twenty-three parts of sodium in one thousand parts of methyl alcohol, and maintain the whole at seventy degrees centigrade for thirty minutes. Distil off the methyl alcohol, digest the residue with one thousand parts of water and two hundred parts of thirty per cent. acetic acid, and filter off, and wash and dry the chlor-brom-indoxyl carboxylic acid ester, which is insoluble in water and is difficultly soluble in most of the common organic solvents. It can be converted into the corresponding indigo coloring matter by boiling three hundred and five parts of it with six thousand parts of water and five hundred and eleven parts of caustic potash for thirty minutes, while passing a current of coal gas through the solution. Then add twelve thousand parts of boiling water to the mixture, and pass air through it at a temperature of one hundred degrees centigrade, until the oxidation is complete. If desired, the saponification can be carried out in the absence of coal gas.

Now what we claim is:—

1. The process of producing symmetrical dichlor-dibrom-indigo, in which the four halogen atoms are in the positions 4.4'.5.5', by saponifying and oxidizing an ester of the corresponding chlor-brom-indoxyl carboxylic acid substantially as described.

2. As a new article of manufacture, symmetrical dichlor-dibrom-indigo, in which the

outside suction heads through said diffusion four halogen atoms are in the positions 4.4' 5.5', which consists when dry of a greenish blue powder, yields a blue solution in cold concentrated sulfuric acid, and a blue solution in hot dimethyl anilin, dyes cotton particularly greenish shades of blue and contains both chlorin and bromin.

In testimony whereof we have hereunto

set our hands in the presence of two subscribing witnesses.

PAUL JULIUS.
VIKTOR VILLIGER.
PAUL NAWIASKY.

Witnesses:

J. ALEC. LLOYD,
W. W. SCHMIDT.

Correction in Letters Patent No. 957,683.

It is hereby certified that in Letters Patent No. 957,683, granted May 10, 1910, upon the application of Paul Julius, Viktor Villiger, and Paul Nawiasky, of Ludwigs-hafen-on-the-Rhine, Germany, for an improvement in "Dichlor-Dibrom-Indigo and Processes of Making Same," an error appears in the printed specification requiring correction as follows: Page 2, line 1, the words "outside suction heads through said diffusion," should be erased; 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 and sealed this 5th day of July, A. D., 1910.

[SEAL.]

F. A. TENNANT,

Acting Commissioner of Patents.

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