

UNITED STATES PATENT OFFICE.

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MANUFACTURE OF BROMINATED INDIGO.

SPECIFICATION forming part of Letters Patent No. 765,996, dated July 26, 1904.

Application filed October 17, 1902. Serial No. 127,721. (No specimens.)

To all whom it may concern:

Be it known that we, ALBRECHT SCHMIDT, Ph. D., and RUDOLF MÜLLER, Ph. D., both citizens of the Empire of Germany, residing at Höchst-on-the-Main, Germany, have invented certain new and useful Improvements in the Manufacture of Brominated Indigo, of which the following is a specification.

The present application relates to the manufacture of bromo-indigo by electrolysis of an aqueous or sulfuric-acid suspension of indigo or indigo-white treated with hydrogen bromid, sodium bromid, or other bromates. However, it is not absolutely necessary to use a diaphragm, as the electrolytical hydrogen has no action in an acid solution on indigo and bromo-indigo. The advantage of this method consists, therefore, in that only small portions of bromin act on an excess of indigo, for with proper choice of the current conditions no excess of bromin can be employed, and in that no regeneration of hydrogen bromid is necessary.

To obtain good yields, it is requisite to operate with not too dilute acids, for otherwise too many products of oxidation are obtained—for example, bromo-isatin. Hydrobromic acid of forty per cent. strength or more or sulfuric acid of fifty to seventy-eight per cent. strength, containing hydrogen bromid, yield good results. Also concentrated hydrochloric acid may be used as electrolyte, if sufficient hydrobromic acid is present; but its use with electrolysis is somewhat inconvenient.

Example: Finely-divided indigo is stirred with hydrobromic acid of about forty per cent. strength or more to a thin paste by means of a high-speed agitator. The electrodes are best of carbon. They may be separated by a diaphragm, hydrobromic acid serving as electrolyte. The electrolysis is conducted, for instance, at about 2.5 volts and three amperes with active stirring until the desired degree of bromination is obtained, which may be calculated from the time and the amperes, for example, to both the mono or dibrom substitution product.

The process is the same with indigo-white. Here, too, a diaphragm may be used or not. Also bromids, such as sodium bromid, may be added during electrolysis.

The brominated indigoes thus obtained resemble in their properties those obtained by dry bromination, German Patent No. 128,575; but whether they are identical with the latter or with that obtained synthetically—for instance, from indoxyl—could hitherto not be observed.

Having now described our invention, what we claim is—

1. The herein-described process for the manufacture of brominated indigo, which consists in electrolyzing indigo by means of a diaphragm in an aqueous suspension treated with hydrobromic acid, substantially as described.

2. The herein-described process for the manufacture of brominated indigo, which consists in electrolyzing indigo without a diaphragm in an aqueous suspension treated with hydrobromic acid, substantially as described.

3. The herein-described process for the manufacture of brominated indigo, which consists in electrolyzing indigo by means of a diaphragm in an aqueous suspension treated with sulfuric acid preferably of twenty to eighty per cent. strength and hydrobromic acid, substantially as described.

4. The herein-described process for the manufacture of brominated indigo, which consists in electrolyzing indigo without a diaphragm in an aqueous suspension treated with sulfuric acid preferably of twenty to eighty per cent. strength and hydrobromic acid substantially as described.

In testimony that we claim the foregoing as our invention we have signed our names in presence of two subscribing witnesses.

ALBRECHT SCHMIDT.
RUDOLF MÜLLER.

Witnesses:

ALFRED BRISBOIS,
JOHANN HARTENSTEIN.