UNITED STATES PATENT OFFICE.

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NITROBENZYLIDEN SULFONIC ACID AND PROCESS OF MAKING SAME.

SPECIFICATION forming part of Letters Patent No. 622,854, dated April 11, 1899.

Application filed December 15, 1897. Serial No. 662,029. (Specimens.)

To all whom it may concern:

Be it known that we, BENNO HOMOLKA, doctor of philosophy, a citizen of the Empire of Austria-Hungary, residing at Frankfort-on-the-Main, and AUGUST STOCK, doctor of philosophy, a citizen of the Empire of Germany, residing at Höchst-on-the-Main, Germany, have invented certain new and useful Improvements in the Manufacture of Ortho- and Para- Nitrobenzylidenanilinsulfonic Acids and Their Homologues, of which the following is a description.

This invention relates to the production of ortho- and para- nitrobenzylanilin and its homologues.

We have found that the nitrobenzylanilinsulfonic acids, described in our American application, dated December 15, 1897, Serial No. 662,028, of the general formula

$$\underset{\text{Nitro-}}{NO_2}\ \underset{\text{Benzyl}}{C_6H_4-CH_2-}\underset{\text{Anilin}}{NH-C_6H_4-}\underset{\text{acid}}{SO_3H}\ \text{Sulfonic}$$

and their homologues lose, under the influence of oxidizing agents, two atoms of hydrogen and are transformed into the nitrobenzylidenanilin sulfonic acids or their homologues according to the following equations:

$$NO_2-C_6H_4-CH_2-NH.C_6H_4-SO_3H+O=$$

O- or para nitrobenzyl-anilin sulfonic acid

$$H_2O+NO_2-C_6H_4.CH=N.C_6H_4-SO_3H.$$

Ortho or para nitrobenzyliden-anilin-sulfonic acid.

$$NO_2-C_6H_4.CH_2-NH.C_7H_6-SO_3H+O=$$

Ortho- or para- nitrobenzyl-toluidin sulfonic acid

$$H_2O+NO_2-C_6H_4.CH=N.C_7H_6-SO_3H$$

Ortho- or para- nitrobenzyliden-toluidin-sulfonic acid.

$$NO_2-C_6H_4-CH_2-NH.C_8H_8-SO_3H+O=$$

Ortho- or para- nitrobenzyl-xylidin sulfonic acid

$$H_2O+NO_2-C_6H_4.CH=N.C_8H_8-SO_3H$$

Ortho or para nitrobenzyliden-xylidin-sulfonic acid.

These nitrobenzylidenanilinsulfonic acids are characterized by a peculiar chemical behavior, as they exist only in form of their metallic salts of the formula:

$$C_6H_4\begin{cases}(1)CH=N-C_6H_4-SO_3M\\(2)NO_2\end{cases}$$

i. e., ortho-nitrobenzyliden-anilinsulfonate salt—where M represents a monovalent metal atom—for instance, Na, K, NH_3, &c.

The free acids do not exist, but decompose completely, in presence of water, into nitrobenzaldehyde and aromatic aminsulfonic acid according to the equations:

$$C_6H_4\begin{cases}(1)CH=N.C_6H_4-SO_3H\\(2)NO_2\end{cases}+H_2O=$$

Ortho-nitrobenzyliden anilin sulfonic acid

$$C_6H_4\begin{cases}(1)COH\\(2)NO_2\end{cases}+H_2N.C_6H_4-SO_3H.$$

Ortho-nitrobenzaldehyd Anilin sulfonic acid.

$$C_6H_4\begin{cases}(1)CH=N.C_7H_6-SO_3H\\(4)NO_2\end{cases}+H_2O=$$

Para-nitrobenzyliden-toluidin sulfonic acid

$$C_6H_4\begin{cases}(1)COH\\(4)NO_2\end{cases}+H_2N.C_7H_6-SO_3H$$

Para-nitrobenzaldehyd Toluidin sulfonic acid.

The nitrobenzylidenanilin sulfonic acids and their homologues therefore form a particularly suitable material for the manufacture of ortho- and para- nitrobenzaldehyde.

We illustrate the practical application of our invention, for instance, as follows: Thirty-three kilograms of ortho- or para- nitrobenzylidenanilinsulfonate of sodium (or the equivalent quantity of the salt of an ortho- or para- nitrobenzyliden-toluidin-sulfonic acid of an ortho- or para- nitrobenzyliden-xylidin sulfonic acid, or of an ortho- or para- nitrobenzylnaphthylamin sulfonic acid) are dissolved in water, whereupon a concentrated solution of 10.5 kilograms potassium permanganate ($KMnO_4$) is slowly introduced while cooling and stirring rapidly. Instead of potassium permanganate the equivalent quantities of other oxidizing agents may be employed—for instance, salts of alkali and alkaline earths of the manganic acid or permanganic acid, manganese dioxid, (MnO_2,) leadperoxid, (PbO_2,) ferric chlorid, (Fe_2Ch_6,) ferric sulfate, $Fe_2(SO_4)_3$, ferricyanid of potassium, ammonium persulfate, &c. It is of advantage to introduce carbonic acid or to add mangnesium sulfate. As soon as the

violet color of the potassium permanganate has disappeared the oxidation is completed. Filtration is done from the precipitated manganese dioxid, and a clear yellow solution of the nitrobenzylidenanilinsulfonate salt or of a salt of the nitrobenzyliden-toluidin sulfonic acid, the nitrobenzyliden or xylidin sulfonic acid, or the nitrobenzyliden-naphthylamin sulfonic acid remains behind. From this solution are obtained the solid salts either by salting out with chlorid of sodium or by evaporation. The salts thus obtained are yellowish powders, soluble in water, insoluble in the other usual mineral solvents. The free sulfuric acids isolated in the usual way from these salts decompose, as already said above, into nitrobenzaldehyd and anilin sulfoacid or toluidin-sulfonic acid, xylidin sulfonic acid, or naphthylamin-sulfonic acid.

Having now described our invention, what we claim is—

1. The herein-described process for the manufacture of ortho- and para- nitrobenzylidenanilin sulfonic acids and their homologues consisting in subjecting ortho- and para- nitrobenzylanilin sulfonic acids or their homologues to oxidation, substantially as set forth.

2. As a new product, the oxidation product of ortho- or para- nitrobenzylanilinsulfonic acids and their homologues, being the salt of a nitrobenzylidensulfonic acid, soluble in water with a yellowish color, insoluble in alcohol, ether, benzene, chloroform, giving on decomposition with diluted minerals acids, nitrobenzaldehyde, substantially as set forth.

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

BENNO HOMOLKA.
AUGUST STOCK.

Witnesses:
HEINRICH HAHN,
ALFRED BRISBISS.