

UNITED STATES PATENT OFFICE.

RUDOLF KNIETSCH AND ROBERT HOLDMANN, OF LUDWIGSHAFEN, GERMANY, ASSIGNORS TO THE BADISCHE ANILIN & SODA FABRIK, OF SAME PLACE.

INDIGO SULFO-ACID.

SPECIFICATION forming part of Letters Patent No. 677,240, dated June 25, 1901.

Original application filed February 6, 1900, Serial No. 4,265. Divided and this application filed February 25, 1901. Serial No. 48,784. (No specimens.)

To all whom it may concern:

Be it known that we, RUDOLF KNIETSCH, doctor of philosophy and chemist, a subject of the King of Prussia, German Emperor, and ROBERT HOLDMANN, a subject of the King of Bavaria, both residing at Ludwigshafen-on-the-Rhine, in the Kingdom of Bavaria and Empire of Germany, have invented new and useful Improvements in Indigo Sulfo-Acid, of which the following is a specification.

Halogen-substitution products of indigo are already known; but all these known products most closely resemble indigo not merely in their property of subliming and the like, but also in yielding a vat from which they can be dyed and in dyeing the various fibers giving blue shades. In our American application, Serial No. 4,265, of February 6, 1900, we have described the preparation of a new halogen-substituted coloring-matter which resembles indigo in the chemical properties in its manner of being dyed and in the fastness of the shades obtained, but which differs from indigo and from the hitherto-known halogen-substitution compounds thereof in that the color obtained by dyeing with it is a brilliant red violet. If this new coloring-matter be treated with fuming sulfuric acid or other suitable sulfonating agent, a soluble sulfo-acid can be obtained, which, however, dyes wool from the acid-bath blue shades. In our present application, which is a division of the above-mentioned application, Serial No. 4,265, of February 6, 1900, we do not wish to claim our new halogen-substituted indigo in its insoluble form; but we do claim our new halogen-substituted indigo in the soluble form of its sulfo-acid.

The new coloring-matter can be conveniently obtained by starting from para-chlor-ortho-nitro-toluene. (See *Berichte*, Vol. 19, page 2240.) This body is oxidized by means of manganese peroxid in sulfuric acid, preferably at a high temperature, so as to obtain para-chlor-ortho-nitro-benzaldehyde. This ortho-nitro-benzaldehyde derivative is then converted by treatment with acetone and caustic soda into our new insoluble indigo coloring-matter. This can be done either directly or the intermediate para-chlor-ortho-

nitro-phenol-lactic-acid-methyl-ketone formed can be isolated and either used as such or after conversion into its bisulfite compound for conversion into indigo by treatment with alkali. After drying the product thus obtained it is treated with such a quantity of fuming sulfuric acid as contains sufficient free sulfuric anhydrid (SO_3) to effect a complete sulfonation of the indigo.

The following examples will serve to further illustrate our invention and the manner in which it can best be carried into practical effect; but the invention is not confined to the examples. The parts are by weight.

Example 1—Oxidation of para-chlor-ortho-nitro-toluene.—Mix together one hundred (100) parts of para-chlor-ortho-nitro-toluene, about one hundred (100) parts of manganese peroxid, (containing about eighty per cent. of MnO_2), and about two thousand (2,000) parts of sulfuric acid, (containing about sixty-three per cent. of H_2SO_4 .) Heat this mixture for from about four (4) to five (5) hours at a temperature of from one hundred and fifteen (115°) to one hundred and thirty (130°) degrees centigrade in a lead-lined vessel furnished with an inverted condenser. When the oxidation is finished, allow the liquid to stand until practically clear. Then separate the acid from the oil and wash the oil successively with water and with a solution of carbonate of soda. Next treat the said oil with sodium bisulfite, so as to obtain the crystalline bisulfite compound of the aldehyde. Dissolve this in water and decompose it with alkali or acid. Collect in any suitable way.

Example 2—Conversion of para-chlor-ortho-nitro-benzaldehyde into para-dichlor-indigo.—Prepare a mixture of one hundred (100) parts of para-chlor-ortho-nitro-benzaldehyde, four hundred (400) parts of acetone, and one hundred (100) parts of water. To this mixture add gradually, while keeping the whole mass cool, two thousand (2,000) parts of dilute caustic-soda lye, (containing one per cent. of NaOH .) The para-dichlor-indigo soon begins to separate out. Collect by filtering, wash, and dry. The new coloring-matter so obtained is a brown-red powder, which on rubbing with a hard body gives an in-

tensely-black metallic streak. Upon heating it sublimes, evolving violet-red vapors, which yield a crystalline sublimate. It is insoluble in the ordinary solvents, but is soluble in
5 boiling nitrobenzene or anilin, (the solutions being violet-red,) from which on cooling it separates out. The new indigo derivative can be dyed like the ordinary indigo from the vat, and it dyes wool and cotton in this way
10 violet-red shades which are fast to washing and to light.

Example 3—Production of a sulfo-acid from para-dichlor-indigo.—To one hundred (100) parts of fuming sulfuric acid (containing
15 about five per cent. of SO_3) or to fifty (50) parts of fuming sulfuric acid (containing ten per cent. of SO_3) add ten (10) parts of the dichlor-indigo obtainable, as in Example 2. Allow the mixture to stand for a few hours
20 at a temperature of fifty (50°) degrees centigrade or for about twelve (12) hours at ordinary temperature. Pour the mixture onto ice, dilute with water, and precipitate the new indigo sulfo-acid with common salt, or
25 after pouring upon ice neutralize the solution with chalk, filter from the calcium sulfate formed, and evaporate the solution of the calcium salt thus obtained to dryness.

Our new indigo sulfo-acid contains chlorin
30 and dyes wool from the acid-bath blue shades.

Its lead, strontium, calcium, magnesium, potassium, sodium, and ammonium salts are easily soluble in water; but the barium salt is difficultly soluble in water. It can be precipitated from a solution of the calcium salt
35 by adding to the same barium chlorid. The free acid itself is also easily soluble in water, the solution being blue, and this solution on addition of caustic soda becomes brown-yellow.
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Now what we claim is—

The new halogen-indigo sulfo-acid, obtainable as hereinbefore described, which contains chlorin and is easily soluble in water
45 the solution being blue, which solution, on addition of caustic soda, becomes brown-yellow, and whose barium salt is difficultly soluble in water, while its calcium salt is easily soluble in water, and which dyes wool from
50 the acid-bath blue, substantially as hereinbefore described.

In testimony whereof we have hereunto set our hands in the presence of two subscribing witnesses.

RUDOLF KNIETSCH.
ROBERT HOLDMANN.

Witnesses:

JACOB ADRIAN,
JOHN L. HEINKE.