

# UNITED STATES PATENT OFFICE.

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

HALOGEN-SUBSTITUTED INDIGO AND PROCESS OF MAKING SAME.

SPECIFICATION forming part of Letters Patent No. 677,239, dated June 25, 1901.

Application filed February 6, 1900. Serial No. 4,265. (No specimens.)

To all whom it may concern:

Be it known that we, RUDOLF KNIETSCH, doctor of philosophy, 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 New Indigo Coloring-Matters, 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.

Our present invention relates to the manufacture of a new halogen-substituted indigo 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 sulfonating agent, a soluble sulfo-acid is obtained which, however, dyes wool from the acid-bath blue shades.

The new coloring-matter can be conveniently obtained, 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 alkali into the new indigo coloring-matter. This can be either done directly or the intermediate para-chlor-ortho-nitro-phenol-lactic-acid-methyl-ketone can be isolated and either be used as such or after conversion into its bisulfite compound for conversion into indigo by treatment with alkali. This conversion can either be effected on the fiber or not.

The following examples will serve to further illustrate our invention and the manner

in which it can best be carried into practical effect, the parts being by weight:

*Example 1—Oxidation of para-chlor-ortho-nitro-toluol.*—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.  $\text{MnO}_2$ ), and two thousand (2,000) parts of sulfuric acid, (containing about sixty-three per cent.  $\text{H}_2\text{SO}_4$ .) Heat this mixture for about four to five hours and at a temperature of from  $115^\circ$  to  $130^\circ$  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 compounds 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-di-chlor-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 one thousand (1,000) parts of dilute caustic-soda lye, (containing one per cent. of  $\text{NaOH}$ .) The para-di-chlor-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 intensely-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 boiling nitro-benzene 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 violet-red shades which are fast to washing and to light. On treatment with fuming sulfuric acid or other sulfonating agent it yields a sulfo-acid, and

in this form it is soluble in water and dyes wool from the acid-bath blue shades.

Now what we claim is—

1. The new coloring-matter para-di-chlor-  
5 indigo which can be obtained from para-chlor-  
ortho-nitro-benzaldehyde and which on heat-  
ing sublimes evolving violet-red vapors which  
yield a crystalline sublimate, and which can  
be dyed like ordinary indigo from the vat  
10 giving violet-red shades and in the form of  
sulfo-acid is soluble in water and dyes wool  
from the acid-bath blue shades substantially  
as described.

2. The process of making coloring-matter  
which consists in treating para-chlor-ortho- 15  
nitro-benzaldehyde with acetone and an al-  
kali, substantially as described.

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

RUDOLF KNIETSCH.  
ROBERT HOLDMANN.

Witnesses:

ERNEST F. EHRHARDT,  
JACOB ADRIAN.