

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.

TETRACHLOR-INDIGO AND PROCESS OF MAKING SAME.

955,410.

Specification of Letters Patent.

Patented Apr. 19, 1910.

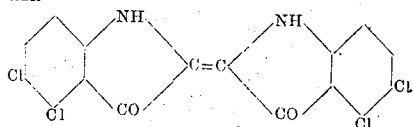
No Drawing.

Application filed November 17, 1909. Serial No. 528,562.

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, the first and third subjects of the Emperor of Austria-Hungary and the second a citizen of the Swiss Republic, residing, respectively, at Ludwigs-
hafen-on-the-Rhine, Germany, have invent-
ed new and useful Improvements in Tetra-
chlor-Indigo and Processes of Making
Same, of which the following is a specifica-
tion.

Our invention relates to the production of
4.4'.5.5'-tetrachlor-indigo. We have invent-
ed a process for its production by the saponi-
fication and oxidation of an ester of 4.5-
chlor-indoxyl carboxylic acid. Thus, upon
operating in this way upon the methyl ester
of 4.5-dichlor-indoxyl carboxylic acid, we
obtain the new product 4.4'.5.5'-tetrachlor-
indigo of a constitution corresponding to the
formula



It consists, when dry, of a greenish blue
powder which yields a blue solution in cold
concentrated sulfuric acid and a blue solu-
tion in hot dimethyl anilin. It differs from
all known tetrachlor-indigos in that it dyes
cotton from a vat exceptionally greenish
shades of blue which are fast against wash-
ing, light, and chlorin. Moreover, the said
shades retain their greenish tint when
viewed by artificial light, whereas the other
tetrahalogen indigos hitherto described as-
sume a reddish or violet-black tint under
similar conditions. Upon being oxidized in
aqueous suspension with nitric acid, our
4.4'.5.5'-tetrachlor-indigo yields 4.5-dichlor-
isatin which can be recrystallized from gla-
cial acetic acid and thus obtained in the
form of red needles which melt at about
247° C.

The following example will serve to illus-
trate 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 convenience, de-
scribe the production of the methyl ester of
4.5-dichlor-indoxyl carboxylic acid.

Introduce, while stirring, two hundred
and ninety-two parts of the methyl ester of
3.4-dichlorophenyl-glycin-2-carboxylic acid
into a solution of twenty-three parts of so-
dium in one thousand parts of methyl alco-
hol, and maintain the whole at seventy de-
grees 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 4.5-
dichlor-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 two hun-
dred and sixty 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
about one hundred degrees centigrade, until
the oxidation is complete. If desired, the
saponification can be carried out in the ab-
sence of coal gas.

Now what we claim is:—

1. The process of producing 4.4'.5.5'-tetrachlor-indigo by saponifying and oxidizing an ester of 4.5-dichlor indoxyl carboxylic acid substantially as described.
2. As a new article of manufacture 4.4'.5.5'-tetrachlor-indigo 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; it dyes cotton particularly greenish shades of blue, and on oxidation in aqueous suspension by means of nitric acid gives rise to 4.5-dichlor-isatin, which 4.5-dichlor-isatin can be recrystallized from glacial acetic acid and thus be obtained in the form of red needles which melt at about 247° C.

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

PAUL JULIUS.
VIKTOR VILLIGER.
PAUL NAWIASKY.

Witnesses:

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