

UNITED STATES PATENT OFFICE.

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THE-MAIN, GERMANY, A CORPORATION OF GERMANY.

DARK-BLUE-VIOLET DYE.

No. 881,158.

Specification of Letters Patent.

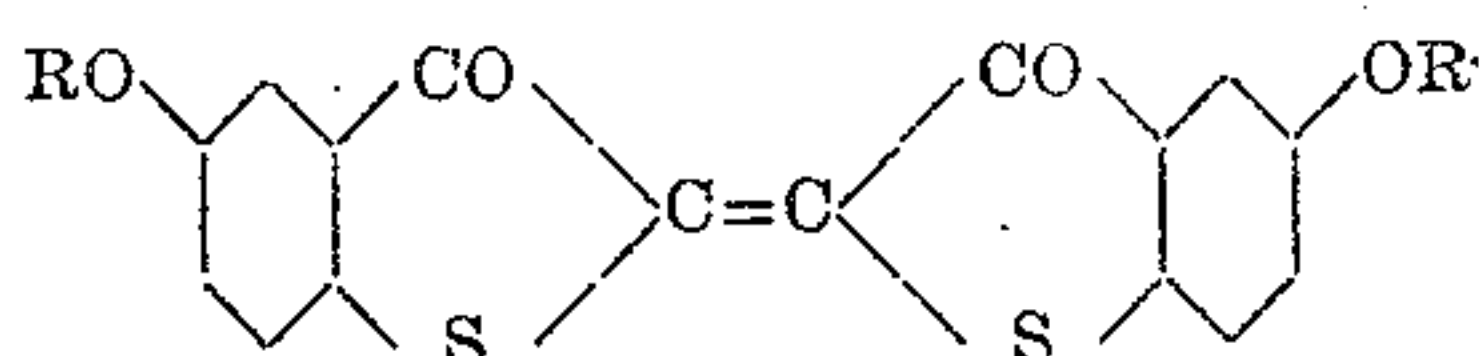
Patented March 10, 1908.

Application filed February 20, 1907. Serial No. 358,420.

To all whom it may concern:

Be it known that we, KARL SCHIRMACHER, Ph. D., and BERNHARD DEICKE, Ph. D., chemists, citizens of the Empire of Germany, and residing at Höchst-on-the-Main, Germany, have invented certain new and useful Improvements in Dark-Blue-Violet Dyes, of which the following is a specification.

This invention relates to new vat dyestuffs the constitution of which corresponds to the formula:



wherein "R" means ethyl and methyl.

The new dyestuffs may be obtained by oxidizing 5-alkyl-oxy-oxythionaphthene carboxylic acids ($RO:S:C = 5:2:1$) obtained from 5-alkyloxyphenylthioglycollic-ortho-carboxylic acids ($RO:SCH_2COOH:COOH = 5:2:1$) by heating with alkali. They are violet powders, insoluble in water, soluble in hot alcohol, benzene, glacial acetic acid and chloroform with a violet color, in concentrated sulfuric acid with a green color. With alkaline hydrosulfite they yield yellow colored vats dyeing wool and cotton dark blue-violet shades.

The method to obtain the new dyestuffs is, for instance, as follows:

Example: 15.3 parts of aminophenolcarboxylic acid ($OH:NH_2:COOH = 5:2:1$) are boiled with 50 parts of glacial acetic acid for 12 hours in a reflux apparatus, half of the glacial acetic acid is then distilled and some water added. The acetylaminophenol carboxylic acid separates. It is obtained in a pure state by crystallizing from water. Then 19.5 parts of this acid are dissolved in 20 parts of caustic soda-lye of 40° Bé. and 200 parts of water, 15 parts of dimethylsulfate being added while stirring. After stirring for some hours, care being taken to keep the liquid alkaline, the methylation is complete; 20 parts of caustic soda-lye of 40° Bé. specific gravity are then added and to effect hydrolysis the whole is boiled in a reflux apparatus till a test portion with hydrochloric acid shows no more a precipitate of unchanged acetyl compound. When cold it is acidified; there are then added 20 parts of hydrochloric acid of 20° Bé. specific gravity and 6.9 parts

of nitrite. The obtained and filtered diazo solution is run at $20-25^\circ$ C. into a solution of 18 parts of potassium xanthogenate and 30 parts of sodium carbonate till no further nitrogen is evolved. Then are added 16 parts of sodium chloracetate and 25 parts of caustic soda-lye of 40° Bé. specific gravity and the whole is boiled. After 1-2 hours it is allowed to cool and on adding a mineral acid the 5-methoxyphenylthioglycollic-ortho-carboxylic acid

$(OCH_3:SCH_2COOH:COOH = 5:2:1)$

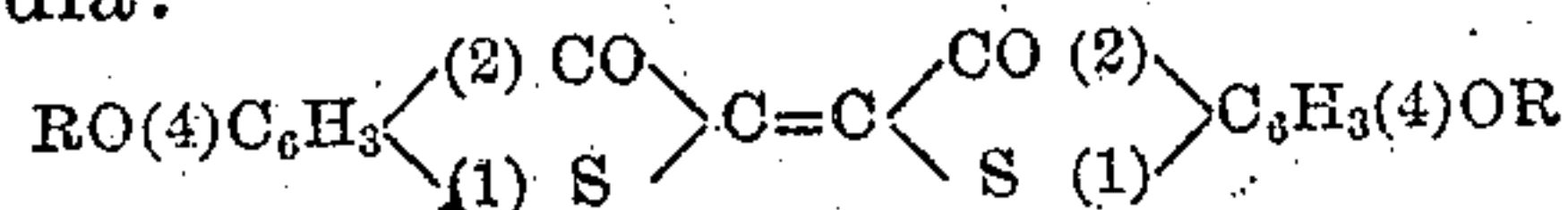
is precipitated. It is a yellowish powder difficultly soluble in cold water crystallizing from hot water in yellowish prisms of the melting point $198-199^\circ$.

To manufacture 5-methoxy-oxythionaphthene carboxylic acid 20 parts of 5-methoxyphenylthioglycollic-ortho-carboxylic acid are heated to $180-200^\circ$ C. for some time with a mixture of 100 parts of caustic soda and 10 parts of water. The fusion becomes yellow and gradually brittle. When cold the mass is dissolved in water and by adding a mineral acid the 5-methoxyoxythionaphthene carboxylic acid is precipitated. It is soluble in acetates and alkalies, yielding, when treated with hydrochloric acid and nitrite, a nitroso compound crystallizing from water in reddish yellow needles. On boiling the afore described 5-methoxy-oxythionaphthene carboxylic acid with hydrochloric acid the 5-methoxy-oxythionaphthene is obtained; it is volatile with steam and crystallizes in white needles.

To convert into the dyestuff, 23 parts of 5-methoxy-oxythionaphthene carboxylic acid or 18 parts of 5-methoxy-oxythionaphthene and 22 parts of caustic soda-lye of 40° Bé. specific gravity are dissolved in 1000 parts of water and then is added a solution of potassium ferri cyanid till no further dyestuff is formed. The dyestuff separates in violet flakes, being, when dry, a violet-black powder. With an alkaline hydrosulfite solution it yields a vat from which it dyes wool and cotton dark blue-violet tints. From the 5-methoxy-oxythionaphthene carboxylic acid a very like dyestuff may be obtained in an analogous manner.

Having now described our invention, what we claim is:—

As products the vat dyestuffs having the formula:



5 wherein "R" means ethyl and methyl, being black violet powders, insoluble in water, soluble in hot alcohol, glacial acetic acid, benzene and chloroform with a violet color, in concentrated sulfuric acid with a green
 10 color; with alkaline hydrosulfite they yield

yellow colored vats dyeing wool and cotton dark blue-violet shades.

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

KARL SCHIRMACHER.
 BERNHARD DEICKE.

Witnesses:

JEAN GRUND,
 CARL GRUND.