UNITED STATES PATENT OFFICE.

KARL ELBEL AND IGNAZ ROSENBERG, OF BIEBRICH, GERMANY, ASSIGNORS TO KALLE & CO., OF SAME PLACE.

PROCESS OF MAKING BLACK SUBSTANTIVE SULFUR DYE.

SPECIFICATION forming part of Letters Patent No. 667,689, dated February 12, 1901.

Application filed January 22, 1900. Serial No. 2,384. (No specimens.)

To all whom it may concern:

Be it known that we, KARL ELBEL, a subject of the King of Prussia, Emperor of Germany, and IGNAZ ROSENBERG, a subject of the Emperor of Austria-Hungary, doctors of philosophy, residing at Biebrich-on-the-Rhine, Germany, (assignors to KALLE & Co., of the same place,) have invented a new and useful Improvement in the Manufacture of New Black Substantive Cotton-Dyes, of which the following is a specification.

Our invention relates to a method of manufacturing substantive cotton-dyes by melting certain para-oxydinitrodiphenylamin derivatives containing a carboxylic group together with sulfur and an alkaline sulfid. The coloring-matters obtained in this manner dye blacks on unmordanted cotton from alkaline baths containing sodium sulfid. They produce shades fast to washing and light. Owing to the presence of the carboxylic group the new dyestuffs form lakes when subsequently treated on the fiber with metallic salts. These lakes resist still better the influence of washing and light than the original dyeings. By this subsequent treatment of dyeings also the depth is increased, while the shade of the color is not materially altered. We have further found that it is of no consequence in which of the two benzene nuclei of the diphenylamin the carboxylic group is contained, but that it is essential for the fastness of the product that the carboxylic group takes up the ortho position either to the imido or to the hydroxy group.

Example 1: In an iron pan heated by means of an oil-bath two hundred kilos crystallized sodium sulfid are melted under addition of a small quantity of water. Seventy-five kilos of ground sulfur and seventy-five kilos of the sodium salt of the oxydinitrophenylamin carboxylic acid (obtained by acting with the dinitroörthochlorbenzoic acid, which fuses at 199° to 200° centigrade, on para-amidophenol in presence of alkaline acetates or carbonates) are then added and well mixed with the melted sodium sulfid. The temperature of the oil-bath is now raised, so that the temperature of the melt gets up gradually to 140° to 150° centigrade within three-fourths of an hour. The melt is then kept at about this temperature until it is perfectly dry and solid, so that it may be ground. After being ground the melt can be employed directly for dyeing purposes. It is a black powder showing a feeble bronzy luster. It is easily soluble in water with greenish-black color, difficultly soluble in alcohol with greenish-blue color. On addition of caustic-soda lye the coloration of the aqueous solution changes to blue-black. Hydrochloric acid precipitates the dyestuff completely in the form of black flakes. In concentrated sulfuric acid it is soluble with greenish-blue color. An addition of water to the solution in concentrated sulfuric acid produces a black precipitate. It dyes a deep black on cotton from an alkaline-salt bath. The dyeings produced with it are very fast and still gain in fastness and in the depth of the shade by subsequent treatment with metallic salts.

Very similar results are obtained if in the above given example the para-oxydinitrodiphenylamin carboxylic acid containing the carboxylic groups in ortho position to the imido group is replaced by other isomeric or homologous para-oxydinitrodiphenylamin derivatives containing the carboxylic group in ortho position to the hydroxy group and which may be obtained by the action of dinitrochlorobenzene ($Cl,NO_2,NO_2;1,2,4$) on para-amidosalicylic acid, ($NH_2,OH,COOH;1,4,5,$) or on amido ortho cresotinic acid, ($NH_2,CH_3,OH,COOH;1,3,4,5,$) or on amido meta cresotinic acid, ($NH_2,CH_3,OH,COOH;1,2,4,5.$)

Now what we claim is—

The process for the production of new black substantive cotton-dyes by melting carboxylated derivatives of paraoxydinitrodiphenylamin together with sodium sulfid and sulfur, substantially as described.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

KARL ELBEL.
IGNAZ ROSENBERG.

Witnesses:
RICHARD GUENTHER,
JEAN GRUND.