

# UNITED STATES PATENT OFFICE.

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ASSIGNORS TO THE ACTIEN-GESELLSCHAFT FÜR ANILIN FABRIKA-  
TION, OF SAME PLACE.

## BLACK SULFUR DYE.

SPECIFICATION forming part of Letters Patent No. 635,168, dated October 17, 1899.

Application filed August 11, 1899. Serial No. 726,864. (No specimens.)

*To all whom it may concern:*

Be it known that we, RICHARD KIRCHHOFF and EMIL HAUSSMANN, of Berlin, in the Kingdom of Prussia, German Empire, have invented new and useful Improvements in Black Dyes; and we do hereby declare that the following is a full, clear, and exact description thereof, which will enable others skilled in the art to which it appertains to make and use the same.

It is well known that by treating certain disubstituted derivatives of benzene, such as para-amidophenol or para-phenylenediamin, with sulfur and sulfids of alkali metals coloring-matters are produced, the so-called "vidal-blacks" of commerce, as described in United States Letters Patents Nos. 532,503 and 532,484. These dyestuffs dissolve in water with bottle-green color and dye cotton dark-green shades, which only by subsequent oxidation are turned black. On the other hand, it has been shown that by melting with sulfur and sulfids of alkali metals certain nitroöxy derivatives of diphenylamin there are obtained coloring-matters which directly produce on the fiber black tints without requiring a subsequent oxidation. A coloring-matter of this kind is brought upon the market under the name of "immedial-black." (Compare United States Letters Patents Nos. 610,541 and 625,717.) We have now found that a quite-unexpected reaction takes place if sulfur and sulfids of alkali metals are allowed to act on mixtures of equimolecular proportions of para-amidophenol and of a nitroöxy derivative of diphenylamin. This reaction does not lead, as might be expected, either to the formation of a mixture of vidal-black and of immedial-black or to the formation of only one of these dyestuffs, but there results an entirely new coloring-matter, which is clearly distinguished from both the dyestuffs mentioned. The new product dyes cotton directly deep-black shades without requiring, like vidal-black, a subsequent oxidation. Also the shades obtained by means of the new coloring-matter are different from those obtained by means of immedial-black, the lat-

ter being more bluish black, whereas our new product yields green-black shades. Furthermore, it is not at all possible to produce the shades which are obtained by means of our new product by simply mixing the above-mentioned coloring-matters separately prepared by the action of sulfur and sulfids on para-amidophenol and on a nitro derivative of diphenylamin. These facts clearly indicate that when mixtures of para-amidophenol and of a nitroöxy derivative of diphenylamin are heated with sulfur and sulfids of alkali metals the two components simultaneously enter into the reaction, a new coloring-matter being formed which is entirely different from the products obtained by treating the two components separately with the same agents.

The following directions will explain in what manner we proceed in order to carry out our invention. Forty-eight parts, by weight, of sodium sulfid, seventeen parts of sulfur, and five parts of water are heated together, and to this mixture is added at 110° to 120° centigrade a mixture of ten parts of dinitroöxy-diphenylamin and four parts of para-amidophenols (equimolecular proportions.) The formation of the coloring-matter commences at about 125° centigrade. The temperature is slowly raised up to 150° to 160° centigrade and maintained for about four to five hours. The dry melt is powdered and can be directly employed for dyeing. The product obtained in this way forms in dry state a grayish-black powder, which readily dissolves in water with a dark greenish-blue color, which on addition of caustic-soda lye turns more bluish. The aqueous solution of the dye is precipitated when mineral acids or acetic acid is added, a brownish-black precipitate being formed. By passing a current of air or carbonic acid through the aqueous solution of the dye a dark-blue precipitate is separated after some time. In concentrated sulfuric acid the dye dissolves with dirty brownish-green color, while in fumingsulfuric acid containing about twenty per cent. anhydride it dissolves with a bluish-black color.



The dye is practically insoluble in the usual solvents, such as alcohol, benzene, ether, and the like.

Our new dye produces directly on unmordanted cotton black shades.

The following alterations may be made in the above example without materially changing the character of the product obtained. For the para-amidophenol we may substitute para-phenylenediamin. Moreover, instead of directly introducing these diamins or amidophenol into the reaction we may equally well use the corresponding nitro derivatives—that is to say, para-nitrophenol, para-nitranilin, para-nitrotoluidin, or para-dinitrobenzene and para-dinitrotoluene—these substances being converted into the amido products by the action of sulfids during the melting process. Further, the quantities of sulfur and sodium sulfid in the above example may be varied within wide limits, and we do not confine ourselves to the figures given in the above example.

Having now described our invention and in what manner the same can be performed, what we claim as new is—

The black dye which results from heating equimolecular proportions of dinitroöxydiphenylamin and para-amidophenol with sulfur and alkali sulfids, said dye being readily soluble in water containing a small portion of alkali sulfid with dark greenish-blue color, which on addition of caustic-soda lye turns more bluish, the aqueous solution yielding on addition of mineral acids or acetic acid a brownish-black precipitate while by introduction of a current of air or carbonic acid after some time a black precipitate is formed, dissolving in concentrated sulfuric acid with dirty brownish-green color, in fuming sulfuric acid with bluish-black color, said dye producing on unmordanted cotton in an alkaline bath black shades of great intensity and fastness.

In witness whereof we have hereunto signed our names, this 21st day of July, 1899, in the presence of two subscribing witnesses.

RICHARD KIRCHHOFF.  
EMIL HAUSSMANN.

Witnesses:

WALDEMAR HAUPT,  
WILLIAM MAYNER.