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UNITED STATES PATENT OFFICE.

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PROCESS OF PRINTING BLACK.

SPECIFICATION forming part of Letters Patent No. 742,530, dated October 27, 1903.

Application filed August 17, 1901. Serial No. 72,356. (No specimens.)

To all whom it may concern:

Be it known that we, EDUARD ULLRICH, Ph. D., a citizen of the Empire of Germany, and VICTOR FUSSGÄNGER, Ph. D., a citizen of the Empire of Austria-Hungary, residing at Höchst-on-the-Main, Germany, have invented certain new and useful Improvements in Processes of Printing Black, of which the following is a specification.

The black hitherto produced by dyers or printers by oxidation or steaming has the disadvantage that it easily turns green, as the action of dilute acids contained in the perspiration or still more that of reducing agents, such as sulfurous acid found in the air, and especially in storehouses, produces a greenish hue, like that of emeraldin, the intermediate product in the formation of the black. This "greening" often occurs to a disagreeable extent in the case of cloths dyed with anilin-black. This drawback has been avoided to a certain degree; but an anilin-black which absolutely does not turn green has not been obtained hitherto. Besides, the anilin-black has this drawback that cotton fiber is easily attacked, and thus becomes rotted by the quantity of acid requisite for the formation of the black.

We have found that primary, secondary, or tertiary amido or amido-oxy derivatives of the diphenylamin series may be substituted for the anilin in making a black and that by oxidizing these bodies on the fiber a full deep black may be obtained which does not become green and does not attack the fiber. The following compounds have proved specially suitable for this purpose: para-amido-para-oxydiphenylamin, para-amido-para-oxy-phenyltolylamin, dimethyl-para-amido-para-oxydiphenylamin, dimethyl-para-amido-para-oxyphenyltolylamin, para-amido-diphenylamin, para-amidomethyldiphenylamin, diamidodiphenylamin, diamido-para-oxydiphenylamin, and dimethyldiamidodiphenylamin; and this invention relates to the manufacture of a black by oxidation or steaming from these and like bodies. Of these compounds only about one-third of the quantity necessary in the case of anilin is required for a full deep black, and whereas in the case of anilin besides oxidizing agents a carrier of oxygen is necessary—such as a solution of a vanadium salt, potassium ferrocyanid, copper sulfid, &c.—the formation of the block occurs here so readily that the use of a carrier of oxygen may be dispensed with, its application, however, not being absolutely excluded. A drawback caused by potassium ferrocyanid, which is commonly used, is avoided by this new process—namely, the formation of Prussian blue, which gives to the black when it leaves the steam a very beautiful bluish tint, which disappears, however, and, owing to the formation of hydrated peroxid of iron, gives place to a less beautiful brown-black when the goods are treated with soap and sodium carbonate. Besides, the new process has the hygienic advantage of avoiding the vapors of prussic acid, which are evolved in the manufacture of the black by the old process. A further drawback, due to the potassium ferrocyanid, consists in the impossibility of printing this compound beside alizarin aluminium colors, as the shades of the latter are much injured by the proximity of the iron compound. As no such compound is used in the new process, the new black may be used together with all colors obtained by steaming. The readily-oxidizable bases used in this process and the small quantity of acid they require to form the black are also of specially technical value, as it allows of the color being directly developed while the piece goods are passed over the drying-cylinders immediately after padding. The slow process of drying in the hot flue, the passing through the steam apparatus, or the prolonged spreading out in the oxidation-chamber are thus avoided.

The new black is very fast to soap, sodium carbonate, light, sulfur, and acid, as well as to alkali and ironing.

The black may be produced on half-silk and silk, as well as on cotton.

Examples.

Black-printing color I.—Thirty grams of

para-amido-para-oxydiphenylamin or the equivalent quantity of any other of the aforesaid bases, one hundred grams of acetic acid of 8° Baumé specific gravity, eight cubic centimeters of hydrochloric acid of 22° Baumé specific gravity, six hundred grams of thickening acetate, thirty grams of sodium chlorate, and two hundred and thirty-two cubic centimeters of water.

Black-printing color II.—Thirty grams of para-amido-para-oxydiphenylamin or the equivalent quantity of any other of the aforesaid bases, one hundred grams of acetic acid of 8° Baumé specific gravity, thirty grams of acetin, six hundred grams of thickening acetate, sixty cubic centimeters of aluminium chlorate of 22° Baumé specific gravity, and one hundred and eighty cubic centimeters of water. After printing the goods are dried, steamed for three minutes, washed, and soaped.

Padding color I.—Thirty grams of para-amido-para-oxydiphenylamin, three hundred grams of hot water, ten cubic centimeters of hydrochloric acid of 22° Baumé specific gravity, fifty cubic centimeters of acetic acid of 8° Baumé specific gravity, one hundred grams of tragacanth-water, (sixty grams per one thousand cubic centimeters,) thirty grams of sodium chlorate, and five hundred grams of water.

Padding color II.—Thirty grams of para-amido-para-oxydiphenylamin, one hundred grams of acetic acid of 8° Baumé specific gravity, thirty grams of acetin, one hundred grams of tragacanth-water, (sixty grams per one thousand cubic centimeters,) seventy cubic centimeters of aluminium chlorate of 22° Baumé specific gravity, and five hundred grams of water. After padding the cloth is dried in the hot flue and steamed in the Mather-Platt apparatus for three minutes, or the black is directly developed on the hot drying-cylinders.

Having now described our invention, what we claim is—

1. The process herein described of producing a fast-black dye on the fiber, which consists in treating the fiber to be dyed with a diphenylamin derivative and then oxidizing said derivative upon the fiber, substantially as set forth.

2. A fibrous material dyed with an oxidation product of a diphenylamin derivative and having the following properties: it is fast to turning green due to atmospheric influence to sulfurous acid, and perspiration, to reducing agents, light, boiling water, soap, feeble alkaline solutions, alcohol, benzene, petroleum ether, ironing and to tendering of the fiber, substantially as set forth.

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

EDUARD ULLRICH.
VICTOR FUSSGÄNGER.

Witnesses:
ALFRED BRISBOIS,
HEINRICH HAHN.