

UNITED STATES PATENT OFFICE.

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PRODUCTION OF ANILIN BLACK ON FIBERS AND FABRICS.

959,516.

Specification of Letters Patent.

Patented May 31, 1910.

No Drawing.

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To all whom it may concern:

Be it known that I, ARTHUR GEORGE GREEN, of The University, Leeds, Yorkshire, England, consulting chemist, have invented certain new and useful Improvements Relating to the Production of Anilin Black upon Fibers and Fabrics, of which the following is a specification.

In the ordinary method of producing an "aged" or "oxidation" black upon textile fibers or fabrics, the material is padded or printed with a solution containing a salt of anilin, usually the hydrochlorid, together with an oxidizing agent, usually sodium or potassium chlorate, and an oxygen carrier, usually a salt of copper or vanadium. Upon the material thus prepared the black is then developed by hanging in a warm chamber more or less saturated with moisture ("aged"). In order to further complete the oxidation, the material is frequently subjected to a final treatment with a hot solution of a bichromate ("chromed"). In applying this process to cotton fabrics, great care is required in order to prevent the weakening or "tendering" of the cotton fiber. The conditions as to humidity and temperature of the aging chamber, the duration of aging and other circumstances have to be carefully and exactly controlled, and even with the exercise of all possible precautions a certain weakening of the material can scarcely be avoided. The cause of this weakening is two-fold: (i) the oxidizing action exerted by the oxids of chlorin produced from the chlorate, which tend to convert the cotton into oxycellulose; (ii) the destructive action of the hydrochloric acid or other mineral acid set free from its combination with anilin.

The present invention relates to a new and improved method of producing anilin black, which is not attended by the above disadvantages, and in which all weakening or tendering of the cotton fiber may be avoided without the exercise of any extreme care. At the same time a fuller utilization of the anilin is rendered possible, the danger of fire from spontaneous inflammation is removed, the risk of injury to the health of the workpeople is greatly diminished, the manufacture is simplified and greater speed of production is attainable. The process may also be applied in cases in which pro-

longed steaming is necessary, as for instance in printing together with tannin colors. It is also applicable to the dyeing and printing of linen, ramie, or silk, or of mixtures of these fibers with one another or with cotton.

The new process is characterized and distinguished from all other known processes of producing anilin black, by the fact that it does not require the presence of an oxidizing agent in the padding or printing mixture, the oxidation of the anilin to the "aged" condition known as emeraldin or to nigranilin being effected solely or mainly by the oxygen of the air. The possibility of dispensing with an oxidizing agent, and thus of avoiding the tendering or weakening of the fiber due to oxycellulose formation, depends on the discovery that a small quantity of a paradiamin or of a para-amidophenol or other substance capable of producing an indamin by condensation with anilin, if added to a mixture containing anilin and a suitable oxygen carrier, such as a salt of copper, greatly accelerates the oxidation of the anilin by atmospheric oxygen. Further whereas in the ordinary processes of producing an "aged" black the quantity of mineral acid employed cannot be materially reduced below the proportion of one equivalent of the latter to one equivalent of base, under the new conditions here set forth a mixture which is basic may be used with satisfactory results for the purpose. Still further, the hydrochloric acid or other mineral acid may be wholly or in part replaced by an organic acid, such for instance as formic acid, without materially affecting the quality of the black obtained. In either case, whether a basic mixture is employed or a mixture containing an organic acid, the tendering of the fiber by free mineral acid liberated during aging or steaming is avoided, even when these operations are unusually prolonged. The action of the paradiamin or para-amidophenol is believed to be a catalytic one, since the quantity employed need only be small in proportion to the anilin, and may be varied within wide limits. These substances bring about the oxidation of the anilin by intermediate formation of complex indamins, from which they are constantly regenerated. In fact, any other compound, such as a nitroso compound or quinone imid, capable of giving rise to in-

damins under the conditions employed, may be used for the same purpose.

As suitable oxygen-carriers the chlorides of copper have been found to give the best results, and in order to prevent the premature formation of oxidation-products in the padding or printing mixture, it has been found preferable to employ the copper in the form of a cuprous salt. A convenient method of effecting this is to add to the mixture cupric chlorid or other cupric salt, together with a sulfite in quantity sufficient to reduce the cupric salt to the cuprous state, and a sufficient amount of a soluble chlorid, such as sodium chlorid, potassium chlorid, or ammonium chlorid, to keep the cuprous chlorid in solution. Mixtures thus prepared are quite stable, and remain clear and colorless on exposure to air for a considerable period. Just as in the ordinary method of producing anilin black, so here also the anilin may be replaced wholly or in part by its homologues such as orthotoluidin or metaxyloidin.

No claim is made to any process for the production of a black from a mixture of anilin and a paradiamin in which the oxidation is effected substantially by means of a chlorate.

The mixtures composed as above are applied to textile fibers and fabrics in the usual manner, namely, by padding or printing. In the latter case the mixture is suitably thickened by means of any of the usual thickening agents. Oxidation is then effected by exposure of the material to air, effected either by passage through the ordinary rapid ager, by hanging in a moist atmosphere, by steaming, or by any other convenient means. Finally it is washed and dried; or according to circumstances it may be subjected to a final treatment with a bichromate either alone or in presence of other materials as at present employed in the after-treatment of an "aged" anilin black, with the object of further oxidizing the emeraldin, or of rendering the black less liable to "green."

Among the various paradiamins and para-amidophenols which are suitable for the purpose of this invention, the following may be specially mentioned:—

Para-phenylene diamin.....	$C_6H_4(NH_2)_2$ [1:4]
Para-phenylene diamin sulfonic acid.....	$C_6H_3(NH_2)_2(SO_3H)$ [1:2]
Para-phenylene diamin carboxylic acid.....	$C_6H_3(NH_2)_2(CO_2H)$ [1:2]
Para-tolylene diamin.....	$C_6H_3(CH_3)(NH_2)_2$ [1:2:5]
Para-amido-phenol.....	$C_6H_4(NH_2)(OH)$ [1:4]
Dimethyl-para-phenylene diamin.....	$C_6H_2(NH_2)_2.N(CH_3)_2$ [1:4]
Diethyl-para-phenylene diamin.....	$C_6H_2(NH_2)_2.N(C_2H_5)_2$ [1:4]
Di-para-amido-diphenylamin.....	$NH_2 \begin{array}{c} \diagup C_6H_4.NH_2 \\ \diagdown \end{array} C_6H_4.NH_2$ [1:4]
Di-para-amido-ditolylamin.....	$NH_2 \begin{array}{c} \diagup C_6H_3.NH_2 \\ \diagdown \end{array} C_6H_3.NH_2$ [1:4]

and their analogues, homologues, or derivatives.

In place of para-diamins and para-amido phenols, there may be used any other substance which under the conditions employed

will give rise to an indamin by condensation with anilin, such, for instance, as one of the following:—

Quinone mono-imid.....	$C_6H_4 \begin{array}{c} \diagup O \\ \diagdown NH \end{array}$	70
Quinone di-imid.....	$C_6H_2 \begin{array}{c} \diagup O \\ \diagdown NH \end{array} \begin{array}{c} \diagup O \\ \diagdown NH \end{array}$	
Quinone mono- or dychlorimid.....	$C_6H_4 \begin{array}{c} \diagup O \\ \diagdown NCl \end{array}$ or $C_6H_2 \begin{array}{c} \diagup O \\ \diagdown NCl \end{array} \begin{array}{c} \diagup O \\ \diagdown NCl \end{array}$	
Para-nitroso-phenol.....	$C_6H_4(NO)(OH)$ [1:4]	
Para-nitroso-dimethylanilin.....	$C_6H_3(NO).N(CH_3)_2$ [1:4]	
Para-nitroso-diethylanilin.....	$C_6H_3(NO).N(C_2H_5)_2$ [1:4]	
Para-amido-phenyl-quinone-mono-imid.....	$C_6H_4 \begin{array}{c} \diagup O \\ \diagdown N.C_6H_4.NH_2 \end{array}$	75
Para-amido-phenyl-quinone-di-imid.....	$C_6H_2 \begin{array}{c} \diagup O \\ \diagdown N.C_6H_4.NH_2 \end{array} \begin{array}{c} \diagup O \\ \diagdown N.C_6H_4.NH_2 \end{array}$	

and their analogues, homologues, or derivatives.

The following examples of suitable compositions for padding mixtures are given in order to illustrate the general method of carrying out this invention; the details may however be varied within wide limits as set forth above.

Example I.—The padding mixture is prepared by adding a solution composed of 48 parts of cupric chlorid, 140 parts of ammonium chlorid, and 14 parts of sodium metabisulfite in 500 parts of cold water, to a solution composed of 50 parts of anilin, 2 parts of paraphenylenediamin, 15 parts of hydrochloric acid (30 per cent. HCl) and 15 parts of formic acid (90 per cent.) in 1,500 parts of cold water.

Example II.—The padding mixture is prepared by adding a solution composed of 48 parts of cupric chlorid, 140 parts of ammonium chlorid, and 14 parts of sodium metabisulfite in 500 parts of cold water, to a solution composed of 50 parts of anilin, 4 parts of paraphenylenediamin, 30 parts of formic acid (90 per cent.) in 1,500 parts of cold water.

Example III.—The padding mixture is prepared by adding a solution composed of 48 parts of cupric chlorid, 140 parts of ammonium chlorid, and 14 parts of sodium metabisulfite in 500 parts of cold water, to a solution composed of 50 parts of anilin, 4 parts of paraphenylenediamin, and 50 parts of hydrochloric acid (30 per cent.), in 1,500 parts of cold water.

What I claim and desire to secure by Letters Patent is:—

1. A process for the production of emeraldin and anilin black upon textile fibers and fabrics, comprising oxidation of an anilin base substantially by atmospheric oxygen in the presence of a copper salt associated with a substance capable of producing an indamin by condensation with anilin.

2. A process for the production of emeraldin and anilin black upon textile fibers and fabrics, comprising oxidation of an anilin base substantially by atmospheric oxygen in the presence of a copper salt associated with a paradiamin.

3. A process for the production of emeraldin and anilin black upon textile fibers and

fabrics, comprising oxidation of an anilin base substantially by atmospheric oxygen in the presence of a copper salt associated with paraphenylenediamin.

5 4. A process for the production of emeraldin and anilin black upon textile fibers and fabrics, comprising the application to the same of a mixture containing an anilin base, an acid, a salt of copper and a substance capable of producing an indamin by condensation with alinin, and afterward
10 subjecting the material to atmospheric oxidation.

15 5. A process for the production of emeraldin and anilin black upon textile fibers and fabrics, comprising the application to the same of a mixture containing an anilin base, an acid, a salt of copper and a paradiamin,

and afterward subjecting the material to atmospheric oxidation.

20 6. A process for the production of emeraldin and anilin black upon textile fibers and fabrics, comprising the application to the same of a mixture containing anilin, hydrochloric acid, a cupric salt, a sulfite, a soluble
25 chlorid and a paradiamin, as paraphenylene diamin, and subsequent subjection of the material to atmospheric oxidation.

In witness whereof, I have hereunto signed my name in the presence of two subscribing
30 witnesses.

ARTHUR GEORGE GREEN.

Witnesses:

THOMAS LAING WHITEHEAD,
ROBERT MILTON SPEARPOINT.