UNITED STATES PATENT OFFICE.

HEINRICH THIES, OF BARMEN, GERMANY, ASSIGNOR OF ONE-HALF TO FRIEDRICH CLEFF, OF SAME PLACE.

PROCESS OF DYEING ANILINE-BLACK.

SPECIFICATION forming part of Letters Patent No. 452,324, dated May 12, 1891.

Application filed February 5, 1891. Serial No. 380,295. (No specimens.)

To all whom it may concern:

Be it known that I, HEINRICH THIES, a subject of the King of Prussia, residing at Barmen Rittershausen, Province of Rhenish Prussia, in the Kingdom of Prussia and German Empire, have invented new and useful Improvements in Printing and Dyeing Aniline-Black, of which the following is a specification.

My invention is based on the discovery that by the employment of hydrofluoric acid (HF) or its salts in addition to the means heretofore used in producing aniline-black in or upon textile fabrics, yarn, or cloth, superior results are produced, as fully pointed out in the following specification and claim.

A large quantity of processes for producing aniline-black in or upon textile fabrics, yarn, or cloth have been proposed—such, for instance, as that proposed by Lightfoot, (Pinkney, *Chem. News* 33, p. 116,) according to which a mixture of fifty grams aniline, fifty grams hydrochloric acid, fifty grams of a solution of chloride of copper of 1.44 specific gravity, twenty-five grams of chlorate of potassium, twenty-five grams of ammonium chloride, and twelve grams of acetic acid is thickened with a liter of starch-paste, and the product thus obtained is printed upon the textile material, and then the printed material is hung up for two or three days in an oxidizing-chamber at a temperature of 30° centigrade, during which time the printed surface, which at the beginning shows no color, assumes a dark-green color. If this color has sufficiently developed, the printed fabrics are brought into a weak alkaline bath, by which a beautiful blue-black hue is obtained. This process produces a beautiful black, but the mixture attacks the metallic parts of the printing-machine, and, furthermore, it injures and weakens the textile fabric. In order to obviate these disadvantages Lauth introduced in place of the soluble chloride of copper the insoluble sulphide of copper. According to his process a mixture of eight hundred grams of hydrochlorate of aniline, three hundred and fifty grams of chlorate of potassium, three hundred grams of sulphide of copper, and three hundred grams of sal-ammoniac is thickened with ten liters of starch-paste. The textile fabric is printed and left in the oxidizing-chamber until a beautiful blackish-green hue appears, when the fabric is washed and finally exposed to the action of a weak alkaline bath.

In order to obviate the harmful effect of the above mixture upon the textile fabric, Koechlin used in place of hydrochlorate of aniline the tartrate of aniline, in the following manner: Two kilograms starch and two kilograms dextrine are boiled in ten liters of water, and two kilograms of aniline, two kilograms of tartaric acid, one kilogram of sal-ammoniac, one kilogram of chlorate of sodium, and immediately before using the mixture one kilogram of sulphide of copper is added, and the mixture thus produced is used for printing, the printed fabric being finally treated as above stated. In place of the copper salts, potassium ferri-cyanide or ammonium ferri-cyanide, and also vanadium salts—such as ammonium vanadate and vanadium chloride—have been used in addition to chlorate of potassium. It has also been proposed to use nitric acid, phosphoric acid, oxalic acid, or hydrobromic acid or their salts in place of the acids or salts above named; but the acids heretofore proposed partly act with insufficient energy and partly with too much energy, partly they volatilize with great difficulty, and the reaction toward its end becomes excessively acid and vehement.

The hydrochloric acid, when applied according to my invention, produces entirely different effects from those above named. Its action consists, chiefly, in thermo-chemical effects and depends, principally, upon its quality of not being liable to decomposition. Of all acids hydrofluoric acid has the largest neutralization heat—that is to say, it develops the largest amount of heat in forming combinations. Its avidity for bases as compared with hydrochloric acid is as one hundred to five. It absorbs on being liberated and on being volatilized a large amount of heat, which paralyzes the increasing energy of the oxidation heat on the fiber, which is a bad conductor of heat. By the reaction and decomposition of the alkaline chlorates hydrofluoric acid does not become decomposed, like the acids heretofore used. As a weak and partly

volatizable acid it assumes in the formation of the black coloring-matter its proportionate share in the reaction. The progress of oxidation therefore does not alternate any more between substitution products of the acid and the products of decomposition produced by the increasing energy of a free acid upon the chlorates. Particularly the formation of a sufficient quantity of chlorine in *statu nascendi* is avoided, and in consequence thereof no substitution products of chlorine are formed, which, according to our present knowledge, produce the well-known greening of aniline-black—that is to say, a greenish hue in the color.

In order to compensate for the weakness of the hydrofluoric acid, I retain a portion of the acids which are at present used in the process, but I limit the energy of these acids to a fixed degree by combining the same for the most part with strong stable metallic bases and eventually with ammonium, whereby the reaction is accelerated by contact and dissociation. By the employment of hydrofluoric acid in the process of oxidizing the aniline the appearance of a surplus of free acids, with the consequent obnoxious secondary reactions, is avoided. The saturating capacity of the aniline at the points of entrance and exit is therefore assumed by the hydrofluoric acid. It produces, even with great latitude in the quantity, a uniform black in the reaction from beginning to end.

By the simultaneous employment of the acids heretofore used in the process it is possible either to avoid or to produce the formation of chlorine, and consequently the process can be carried out so as to produce at once either a stable black or a black the greening of which can be exactly gaged, as business may demand.

The following is an example of the mixture, which can be used successively for dyeing mixed fabrics of cotton and silk: carbonate of copper, two grams; bicarbonate of ammonium, four grams; hydrochloric acid of thirty per centum in solution, twenty-five grams. To this solution is added hydrofluoric acid of sixty per centum, fifty-five grams, diluted with two hundred grams water. To this mixture are added one hundred and forty grams of aniline oil and sixty grams of chlorate of sodium dissolved in a sufficient quantity of water so that the entire mixture fills a liter. A corresponding quantity of the textile fabric is saturated with this liquid, and after having become saturated the fabric is dried and oxidized and finally washed.

For woolen fabrics the proportion of the acids and oxidizing agents in the mixture must be changed. For printing with aniline-black I use the well-known vanadium, cerium, iron, chromium, or copper compounds with the chlorates; but for a portion of the acids I substitute fluoric acid.

The aniline-black produced according to my invention with the acid of hydrofluoric acid is deep black in looking down, but brown in looking overhand. It is not changed by sulphurous acid or by any other acid. It does not show the basic qualities of the ordinary aniline-black, and for this reason it combines more readily with tar colors, which can be used for shading. The principal advantage of my invention, however, is that the fiber retains its natural qualities. The luster of the silk is not dimmed, wool remains soft, and vegetable fibers are scarcely affected.

My invention is also of advantage in the process of producing black, brown, or gray colors from aniline or its homologues and from naphthylamine.

What I claim as new, and desire to secure by Letters Patent, is—

The within-described process for dyeing or printing animal or vegetable fiber, yarn, or cloth in black and analogous colors, which consists in exposing such fiber, yarn, or cloth to the action of aniline oil in the presence of hydrochloric acid, an alkaline salt, and hydrofluoric acid, substantially as described.

In testimony whereof I have hereunto set my hand in presence of two subscribing witnesses.

HEINRICH THIES.

Witnesses:
WM. ESSEMREIN,
RUDOLPH FRICKE.