UNITED STATES PATENT OFFICE.

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IMPROVEMENT IN DYEING YARNS AND FABRICS IN ANILINE-BLACK.

Specification forming part of Letters Patent No. 193,158, dated July 17, 1877; application filed March 13, 1877; patented in England, October 21, 1874, for fourteen years.

To all whom it may concern:

Be it known that I, WILLIAM JULES SAMUEL GRAWITZ, of Paris, France, chemist, have invented Improvements in the Production of Aniline Blacks and Grays, and in the application of the same for dyeing textile materials; and I do hereby declare that the following is a full, clear, and exact description of the same.

This invention relates to certain chemical reactions, having for object the production from aniline of a series of black colors, or shades bordering on black, and also to the processes employed in applying the same for dyeing textile materials.

The novel chemical reactions of my invention consist in the concurrent action on aniline-oil or on its salts, of certain metallic salts and soluble chromates or bichromates or chlorates, without the necessity of exposure to air. The action of the metallic salts may either precede or follow that of the chromates or bichromates, and both may be performed with or without the aid of heat.

I will proceed to describe the three principal modifications of my invention in the dyeing of textile materials.

The first modification consists in the formation of a complex base, containing both aniline and a metal, this base being obtained by precipitating certain metallic salts by means of aniline-oil. These complex bases redissolve in acids.

The second modification consists in forming a bath containing the elements of a double salt of aniline and of metal. For example, I place together in the bath equal equivalents of perchloride of iron and hydrochlorate of aniline.

The third modification consists in forming a bath containing the elements of an aniline salt combined with the metal—that is to say, salts of aniline with a metallic acid. This latter modification includes the formation, by double decomposition in the baths, of ferro and ferri cyanides of aniline, of chromates and bichromates, manganates and permanganates, tungstates, vanadates, and bivanadates of aniline.

These complex bases, these double salts of aniline and of metal, these salts of aniline with a metallic acid, have all the property of enabling the aniline to gradually oxidize with the greatest facility, produce black, or shades bordering on black, according to the degree of oxidation.

The application to dyeing textile materials of the above series of reactions and of processes may be effected in one, two, or three baths.

The following is the method of dyeing with three baths. The complex bases above referred to are precipitated on the materials to be dyed, by first impregnating with aniline then with the metallic salt, the textile matters being carefully drained between each bath. The black is then developed by introducing the textiles into a bath of soluble chromates, bichromates, or chlorates.

In operating with two baths in two distinct ways, the textiles are placed in baths containing either the elements of a double salt of aniline and of metal, or the elements of a salt of aniline with a metallic acid. The textiles become dyed in this bath of a gradually deepening green color, whether the bath be cold or heated, and they may be thoroughly rinsed without removing the dye. The aniline is then peroxidized and the black developed by placing the matters to be dyed in a bath of soluble chromate, bichromate, or chlorate.

In dyeing with a single bath I place therein either altogether or successively the whole of the constitutive elements of the black, the bath being cold when the textile materials are introduced. The reaction is allowed to commence at the ordinary temperature and the bath is then gradually raised to about 100° centigrade. When chromates are used the reaction should be allowed to continue for about half an hour before heating; otherwise a gray shade would be produced, and the color would be precipitated in the bath.

The latter method of operating in a single bath greatly facilitates dyeing piece-goods.

The aniline salts with a metallic acid which give the best results are those in which the metallic acid is chromic acid. With a bath containing (by reason of a double decomposition) the elements of chromate of aniline without an excess of chromic acid, the textiles will only be dyed of a deep green, which is changed to blue-violet by means of an alkali,

in exactly the same manner as with perchloride or nitrate of sesquioxide of iron. By peroxidizing with a bath of soluble bichromate or chromate, the green is changed to a black. Black may be at once produced if a sufficient quantity of the chromate or bichromate is placed in the bath.

When chlorate is used, the quantity of acid in the bath should be sufficient to saturate the base combined with the chloric acid.

When employing chromates and bichromates it is necessary not only to saturate the base combined with the chromic acid, but also to saturate the oxide of chromium resulting from the reduction of the chromic acid.

The metals whose salts are suited to one or the other of the above reactions are those which are susceptible of two degrees of oxidation, and readily converted from the one to the other by oxidation or reduction, and the following more particularly have a very energetic action, viz: iron, copper, manganese, cerium, chromium, nickel, cobalt, tungsten, uranium, and vanadium.

I reserve the application of all mineral or organic acids in combination either with aniline or with metals, or in a free state in the dye-bath.

The quality of the color is dependent on the nature of these acids, their proportion in the bath on the metals employed, and also on the temperature of the bath.

I will here give three examples of the method of dyeing cotton in hanks.

First example: I form a bath, A, containing, for one liter of water, aniline, thirty cubic centimeters; hydrochloric acid, ninety cubic centimeters, at 22° Baumé; nitrate of sesquioxide of iron, forty cubic centimeters, at 40° Baumé.

I form a second bath, B, containing from ten to twenty grams of bichromate of potash per liter.

The cotton, in small portions at a time, is dipped in the bath A, (which may be either cold or tepid,) and after being slightly wrung, but not rinsed, is placed in the bath B, where it digests for about three hours. The cotton on leaving bath A retains sufficient acid to decompose the proper quantity of bichromate.

I then recommence the same series of operations, mordanting in bath A, and peroxidizing in bath B until the obtained shade is sufficiently laid on. Three such double passages through the baths will generally suffice.

The dyeing is complete when a sample, on being dipped in a weak warm solution of carbonate of soda, remains of a chestnut color without changing to a violet.

Second example: For every ten kilograms I take of water one hundred and fifty liters; hydrochloric acid, four liters; aniline, one liter; bichromate of potash, one kilogram, five hundred grams.

I dip the cotton, after well boiling, in this bath, work it for about three quarters of an hour, after which I rinse, and immerse it in a boiling bath containing one gram of persulphate of iron, for example, per liter, slightly acidulated, for about a quarter of an hour.

Third example: I take, for one hundred kilograms of cotton, water one hundred and fifty liters; muriatic acid, at 22° Baumé, four liters; aniline, one liter; bichromate, two kilograms, two hundred and fifty grams.

The cotton is introduced into a cold bath, worked for three quarters of an hour, after which the temperature is gradually raised to 100° centigrade, and kept thereat for at least one quarter of an hour.

The blacks obtained by these three methods are insoluble in cold sulphuric acid of 66° Baumé, and will not turn green under the action of sulphurous acid. They are, in fact, true blacks. By dilution, they give greys, having the same properties. With a single cold bath I obtain what I term shades bordering on black or greys, these colors changing to a green under the action of sulphurous acid.

In this manner may be dyed cotton, flax, wool, silk, feathers, and all vegetable or animal textile matters generally. For dyeing piece goods it is preferable to use a single bath, or at least to revive the first bath with a salt of aniline with a metallic acid, as in the second example, before given.

The proportions of the elements indicated are those which have been found to give the best results, although I do not intend to limit myself thereto.

I claim—

The herein-described process of dyeing vegetable or animal textile materials of black and grey colors, or shades bordering thereon, by slow concurrent progressive reaction on the textile fibers themselves, of aniline salts and metallic oxidizing salts or acids, without exposure to the air, and with or without heat, with a subsequent peroxidation by means of chloric or chromic acid, substantially as set forth.

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Witnesses:
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