UNITED STATES PATENT OFFICE.

ALFRED PARAF, OF MULHOUSE, FRANCE, (AT PRESENT RESIDING IN MANCHESTER, ENGLAND.)

IMPROVEMENT IN DYEING YARN, &c.

Specification forming part of Letters Patent No. **52,942**, dated February 27, 1866.

To all whom it may concern:

Be it known that I, ALFRED PARAF, of Mulhouse, in the Empire of France, at present temporarily residing at Manchester, England, manufacturing chemist, have invented or discovered certain Improvements in Printing and Dyeing Textile Fabrics and Yarns; and I do hereby declare that the following is a full and exact description thereof, and of the way in which my improvements are to be carried into practical effect.

Chloric acid has hitherto only been used in dyeing and printing in the state of chlorate of potash, which was mixed with colors or the dyeing-bath to oxidize, and also for preparing cloth to be printed with salt of protoxide of iron or tin.

When chlorate of potash is used for preparing textile fabrics or mixed with coloring-matter or dyeing-bath it crystallizes very easily in consequence of its extreme insolubility, the consequence being that, the outsides only of the crystals being in contact with the substances to be oxidized, these substances are liable to oxidize too much round about those crystals and not enough at a certain distance from the crystals, which causes great inconvenience.

I obviate this in the following manner: Instead of using chloric acid combined with potash, I combine it with other bases which form salts more soluble or less liable to crystallize—such, for instance, as soda, oxide of lead, barytes, strontian lime, and similar salts.

As the chloric acid of the chlorate ought to be set free to enable it to oxidize, it will be easily perceived that I can raise the base of the chlorate of baryta, lead, strontian, or lime more easily than chlorate of potash, which does not give as they do sulphates or other salts nearly insoluble.

I have already applied a reaction of the potash to facilitate the decomposition of the chlorate of potash, and thus dispense with a great part of its defects. For that purpose, instead of decomposing by the usual acids—as oxalic, tartaric, nitric, and similar acids—I decompose by hydrofluosilicic acid, which gives me a salt of potash near insoluble, sets the chloric acid free, and consequently acts more completely and naturally prevents the making of crystals.

In consequence of the greater solubility of the chlorate and more complete setting at liberty of the chloric acid, I can put a larger quantity in contact with the substances to be oxidized. I obtain more complete oxidation for steam colors, such as catechu brown, the aniline black, and similar colors, which are produced more advantageously.

I can add to a color containing chlorate of potash or other bases one or more chlorates of different solubility to chlorate of potash. The result will always be better than with chlorate of potash alone, and this advantage will make part of my present improvements. In fact, whatever plan shall be employed in printing or dyeing, the chlorates more soluble or less liable to crystallize than potash will always form a leading part of my invention. It will be the same thing if hydrofluosilicic acid is used to decompose the chlorate of potash.

When I impregnate the fiber or fabric with a chlorate and put the said goods to be printed or dyed in contact with the coloring-matter which contains the necessary substance to decompose the chlorate, as hydrofluosilicic acid if it be chlorate of potash or barytes, sulphuric and similar acids; if it is chlorate of lime, barytes, strontian, or lead—in a word, an acid or acid-salt or other salt or body which will decompose the chlorate. I can press the oxidizing action of the chlorate by adding to the coloring-matter a salt of iron.

I also find that the chlorites and hypochlorites oxidize still more quickly and more completely than the chlorates, and I reserve to myself the use of the chlorites and hypochorites.

As by the decomposition of the chlorate it forms some chlorhydric acid, which, in some instances, does harm by altering the fiber, I take all or a part of the chloric acid, in the state of chlorate of lead, or add some fluosilicate of lead, whereby all or part of the chlorhydric acid is transformed into harmless chloride of lead.

In some cases, as the acid contained in the color produces chlorhydric acid of the chlorate, that may be the acid used to decompose the chlorate notwithstanding other colors being printed at the same time. It produces some white edges and the colors become more

pale. This happens especially in printing an acid color to the chlorate in a design of several colors where some are red, rose, violet, or chocolate to be dyed in madder, or some buffs, orange, chrome, and similar colors.

In some cases where the acid contained in the color—either chlorhydric acid produced by decomposition, the chlorate, or the acid used to decompose the chlorate—injures the colors at the same time, I have two methods of refixing on the fiber the metallic oxide which the acid will have dissolved: first, by dumping in an alkaline liquid silicate of soda or potash to a degree of concentration sufficient to precipitate the mordant dissolved at 7½° to 30° Twaddell; secondly, by exposing the fiber or material after dyeing and before dunging to ammoniacal vapor.

In applying the use of soluble chlorate to aniline black I have found the following process to give very good results: I prepare the textile fabric to be dyed or printed in a solution of chlorate of soda at 10° to 12° Twaddell, dry without washing, and print or pad upon it the following color: two pounds aniline-black liquor, three pounds water, two pounds white starch, two pounds gum-dragon paste, one pound brown British gum, seven ounces lamp-black. Boil well together and cool down. Age in a cold room for one or two days; but if pressed for time the black can be produced in a few hours by running once or twice through an aging-machine.

The aniline-black liquor I prepare by dissolving one part of crystals of chloride of aniline in one part of hydrofluosilicic acid at 10° Twaddell, and add two per cent. of chloride of iron.

This black has over the other aniline blacks the following advantages: First, the color, when made ready for printing, remains undecomposed for any length of time; secondly, acts neither on steel doctors or copper rollers; thirdly, the back cloths can be bleached any time after printing; fourthly, the black is produced very easily; fifthly, gives a shade of black unknown till this day; sixthly, does not tender the cloth, at least any more than a common madder black; seventhly, does not form any white edge with any color printed near it; eighthly, it adapts itself perfectly to all colors to be dyed in garancine madder or alizarine, chrome, orange, catechu brown, &c.; ninthly, is black before printing, and therefore shows all faults produced by bad rollers or doctors and allows the imperfect printing to be bleached before the production of the indelible color; tenthly, does not turn green by exposure to the air, as is the case with other aniline blacks.

I also use chloric acid or hypochloric acid combined with aniline or its homologues for the production of black and gray colors. I decompose sulphate or oxalate of aniline or similar salts with chlorate or hypochlorate of barytes, lead, lime, strontian, soda, so as to produce by double decomposition chlorate or hypochlorate of aniline or its homologues, which, printed or dyed upon fabrics or yarns, produces fast black or gray by aging. The addition of one or two per cent. of chloride of iron to the salt of aniline in this case much improves the result.

Suppose all the animal matters do not take well, or even do not take some colors at all in which the chlorate acts an important part and which take well upon a vegetable matter, but not on such substances as wool or silk, the addition even of copper to the color or in the dyeing-bath, in this case, will be of no use, as the black will not be good. I surmount this difficulty as follows: I combine with the animal matter some metallic salts, such as copper or others capable of assisting the decomposition of the chlorate, and then the animal substance will take the black which the cotton has already taken. Sometimes the solution of the salt of copper combines with the animal matter in a cold state, as for light wool or silk; but for heavy wool, as goat's wool, I often make it very hot, sometimes to ebullition, with a solution of salt of copper. This operation being completed, I wash to raise the part of the salt of copper not combined with the animal matter.

If the animal matter is to be printed with the salt of aniline, I dry it after washing, and then print the same black as I print upon cotton. Drying or not in the dyeing process is immaterial. It is not to aniline alone that this means is applicable for fixing upon animal matter the chlorate preparations which are not easily applied by other means. This mode of preparing the animal matter constitutes a portion of my invention, whether any color to which it is to be applied immediately, or the result shall be to give an animal matter proper or more capable of taking a cotton chlorate color; but I may observe that I get quicker results in combining on the animal matter chloric and chromic acid with the copper, and I proceed as follows: I dissolve one pound of sulphate of copper in one gallon of water, then add half a pound of chlorate of soda and half a pound of bichromate of potash, filter the liquor and prepare the animal fiber in it, wash well, and then dye in aniline-black liquor—that is to say, in one part of the black liquor mixed with two or two and a half parts of water. After dyeing, if the shade is not deep enough, I pass again in the chromo-chlorate-of-copper preparation, then again in the aniline liquor. In this case I give no chloride of iron in the aniline-black liquor.

I may also observe that I consider that the great analogy which exists between the sodates, bromates, and the chlorates will allow nobody the right of substitution of those salts for the chlorate without infringing the present patent.

I have used in this specification the words "fiber" and "matter." By "fiber" I understand all textile substances, such as cotton, linen, wool, goat's wool, silk, &c., under any

state that those textile fibers may be—that is to say, bleached or gray, spun, woven, carded, felted, &c. By "matter" I understand all matters able to take color, such as wood, paper, skins, &c.

I claim—

1. As oxidizing agents in dyeing and printing, the use of the oxygen compounds of chlorine more soluble than those combined with potash, such as chlorate of soda, chlorate of ammonia, chlorate of barytes, chlorate of strontian, chlorate of lead, chlorate of lime, chlorate of magnesia, chlorate of alumina, chlorate of zinc, chlorate of nickel, chlorate of copper, chlorate of chrome, chlorate of manganese, and chlorate of potash, when decomposed by hydrofluo silicic acid, either for preparing textile fibers to be printed with steam colors or aniline black, catechu brown, and similar colors, or by mixing them with colors and dyeing-bath to oxidize, and to the aniline-black color, in order to hasten the oxidation, I find advantage in adding two and a half to three per cent. of a salt of protoxide of iron or copper, and print such colors upon cloth prepared in one or more of the above-mentioned soluble chlorates.

2. The use of the chlorites and hypochlorites in the place of the chlorates in dyeing and printing.

3. The preparation of animal fibers in copper salts mixed with chloric and chromic acid salts to enable them to receive aniline blacks or other similar colors for dyeing and printing.

Done at Manchester, England, this 29th day of December, 1865.

ALFRED PARAF.

In presence of—
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