

UNITED STATES PATENT OFFICE.

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ANILINE-BLACK.

SPECIFICATION forming part of Letters Patent No. 409,822, dated August 27, 1889.

Application filed February 15, 1889. Serial No. 299,984. (No specimens.)

To all whom it may concern:

Be it known that I, JOHN BRACEWELL, of North Adams, in the county of Berkshire and State of Massachusetts, have invented a new and useful Improvement in Aniline-Black Color, of which the following is a specification.

My invention relates to the production of aniline-black color upon cloth; and it consists in a certain new and useful mode of compounding and developing the same, either alone or in connection with patterns printed thereon either as a resist or discharge, substantially as hereinafter described and claimed.

Heretofore aniline-black color has been produced upon cloth by the oxidation of the aniline when applied thereto; but its production has been attended with certain disadvantages when this oxidation was accomplished by the use of live steam or steam under pressure, because this process impaired the fiber of the cloth or made it tender where the aniline color came in contact with it, and in consequence the goods when blotched or padded with the color were usually subjected to the wet steam or other aging process at a comparatively low temperature to avoid this difficulty. In this steam-aging process the steam is discharged into an open-air space and comes in contact with the goods in the shape of wet steam of such comparatively low temperature, and this aging process impairs the colors of the pigments used in the resist or discharge patterns printed thereon.

Another difficulty in the employment of aniline-black arose from the practical impossibility of employing and developing it on goods upon which a pattern had been previously printed with a resist by the use of live steam or steam under pressure without "tendering" the goods, whereby the superior sharpness of outline in shade of the black edge against the pattern, or vice versa, which is given by steaming the goods under pressure, was not produced and at the same time the strength of the fibers preserved. Again, if the resist was mixed with pigment colors, the steaming of the latter to set them firmly and at the same time develop the aniline-black was accompanied by this disadvantage of tendering the goods.

A third difficulty with the aniline-blacks heretofore known was that after the aniline color was applied to the goods and dried it oxidized so rapidly that there was not time afforded before oxidation to print on patterns with a discharge mixture, white or colored, in a certain economical and practical manner, it being necessary to employ the greatest care in drying the cloth and to hasten it from the drying apparatus to the printing-machine and print the discharge on at once, thereby making one process wait on the other, and causing loss of goods and expense if any accident happened to the printing-machine or to the process of drying.

By my new mode of forming and compounding aniline-black color I am enabled to produce one which does not oxidize so rapidly in drying, and so allows time for a discharge pattern to be printed thereon before oxidation, which can be developed by steam under pressure without tendering the goods and simultaneously with the setting of the colors of the discharge or resist thereby, and leaves the pigment colors in the resist or discharge of superior brilliancy, and which, with a white discharge or resist, gives by this mode of development a superior sharpness to the outline of the colored pattern on the aniline ground in shade or line of both the color and ground against each other.

My invention consists in the discovery that when a certain proportion of ferro-cyanide to the aniline is used, much larger than has heretofore been employed in the compounding of aniline-black color, the oxidation of the aniline will be so retarded that the above effects are accomplished, and that under steam-pressure it will proceed in such a manner as not to tender the fiber of the cloth. Moreover, when this proportion of ferro-cyanide is employed with the aniline and a proper proportion of chlorate of potash, the black produced by the oxidation of the aniline is of superior quality, and the aniline color may be blotched, padded, or dyed entirely through the fiber of the cloth and developed perfectly, without injury to the fiber, by using steam under pressure—a result which I believe to be new.

Heretofore so-called "steam" aniline colors

have usually been printed on only one side of the cloth, and the tendering of the parts of it with which they came into contact when developed by steaming was not so material
5 as it is when the cloth is saturated to any considerable depth by the color.

In order to form my aniline color I proceed as follows: I mix, cold, twelve gallons of the ferro-cyanide paste given below with four gal-
10 lons of the solution of aniline-salt crystals given below, and add thereto four pints of aniline-oil, when the color is ready for use. The aniline-oil is added to neutralize any free acid which may exist in the aniline solution
15 from the aniline salts, and it may be omitted if that solution contain no free acid. This preparation of the solution without free acid is of the utmost importance, as its presence in the color will cause it to act upon the fiber
20 of the cloth under the steaming hereinafter described and destroy or seriously injure it. The ordinary salts of aniline of commerce contain free acid, and the use of the aniline-oil is indispensable, unless the salts of aniline
25 have been specially prepared so as to be free from acid. The presence of the free acid in the color when applied to the cloth will also prevent the ferro-cyanide used in the proportions stated from retarding the oxidation of
30 the aniline on the cloth, as before described. This aniline color may be padded into the cloth or printed thereon, as desired.

The ferro-cyanide paste is formed as follows: Take forty-five gallons of water and
35 dissolve in it seventy pounds of ferro-cyanide-of-soda crystals and twenty-three and three-fourths pounds of chlorate of potash. Add twenty pounds of corn-starch and boil till thickened, and cool. The corn-starch may be
40 omitted or added in greater or less quantity as the printing, padding, or saturating of the cloth or yarns with the aniline color may require.

The solution of aniline salt is prepared as
45 follows: Dissolve sixty pounds of aniline-salt crystals in ten gallons of hot water and cool. Instead of the salts of aniline, an equivalent amount of aniline-oil neutralized with hydrochloric acid may be employed. The aniline-
50 oil might be added to the solution of aniline salts, if preferred. If the oil be neutralized by the acid, an excess of oil must be used to avoid the presence of free acid.

The proportions of the ferro-cyanide to the
55 aniline salts in the above color may be varied, as I have only given the proportions I prefer to employ; but care should be taken that the proportion of the ferro-cyanide to the aniline shall never be less than eighty
60 per cent. of the latter in any given quantity of color. Instead of ferro-cyanide of soda, the corresponding salt of potash or ammonia or other base may be employed, due allowance being made to preserve the equivalent
65 proportions of the ferro-cyanide in strength under those forms. The insoluble chromates

or chlorate of alumina might be employed instead of ferro-cyanide.

I employ in the above formula, which I prefer, about one hundred and eight parts of
70 ferro-cyanide to each one hundred parts of aniline salts. When the proportion of ferro-cyanide to aniline salts in the color exceeds eighty per cent. of the latter, I have found
75 that the ferro-cyanide neutralizes or substantially neutralizes the aniline, forming a ferro-cyanide of it, so that an injurious amount of chlorate of aniline cannot be formed in the color, and that a rapid process of the oxidation of the aniline is prevented when exposed
80 to the action of steam under pressure, which rapid process substantially tenders or impairs the strength of the goods, if permitted.

To insure the complete neutralization of the aniline and the retarding of the forma-
85 tion of chlorate of aniline in the color, I prefer to employ the proportions I have given, and a greater amount may be employed, if preferred, as it is upon the neutralization of the aniline by the ferro-cyanide and the pre-
90 ventation thereby of the formation of an excess of chlorate of aniline in the color that the superior qualities of my color depend.

The proportions of ferro-cyanide given and referred to above are of the normal strength
95 of crystals, and if the desiccated form of ferro-cyanide of soda be employed, which has greater strength, a less amount may be employed—say, instead of a minimum of eighty
100 pounds of the crystals, fifty pounds of the desiccated, or more, to each one hundred pounds of aniline salts, according to strength. A sure test of the amount of ferro-cyanide
105 present, and one which determines whether it has substantially neutralized the aniline, is the capacity of the aniline to oxidize by the ordinary process of aging the goods, as goods treated with my black color require steaming
110 to oxidize and develop it. If it be found on trial that the aniline is oxidized by aging, then more ferro-cyanide must be added, for the salts or solution of it used must necessarily have been of less strength than what I
115 have referred to in giving the proportions above stated, and it has not neutralized the aniline. Different preparations of ferro-cyanide may vary in strength—as, for instance, when a solution of it is used instead of the salts—and in such cases the quantity
120 must be ascertained by trial which should be employed.

The proportion of chlorate of potash used in the above color may also be varied with relation to that of the aniline, using between
125 thirty and sixty-five pounds to each one hundred pounds of aniline salts, as its proportion is not so material, the formation of chlorate of aniline and consequent rapid oxidation and development of the aniline color being retarded by the ferro-cyanide, as
130 above explained, whether the chlorate of potash be present in greater or less degree.

When, however, the steam under pressure is applied to the color and sets free the aniline from the ferro-cyanide, and the latter carries over the oxygen from the chlorate of potash to the aniline, (by means of its metallic properties,) sufficient chlorate of potash should be present to oxidize and develop the aniline-black in a superior manner, which I have ascertained by experiment to be at least thirty per cent., by weight, of the aniline salts used.

Ferri-cyanide of soda may be employed to form the described color in lieu of ferro-cyanide, in which case the amount of chlorate of potash may be diminished in proportion, as none of it in that case will need to be taken up after the color is mixed to change ferro-cyanide into ferri-cyanide, and the amount of such diminution of the chlorate when ferri-cyanide is used will be about four and nine-tenths parts to every one hundred parts of ferro-cyanide.

If it is desired to produce a white pattern on the aniline-black ground, it may be accomplished by printing the pattern on the cloth before the aniline-black is applied with a resist mixture, which is made up as follows: gum substitute, four pounds; acetate of soda, four pounds; water, eight pounds; dissolve and mix thoroughly in the water. If the resist is to be colored, mix with the acetate of soda albumen, either egg or blood, in place of the gum substitute, and a pigment of the desired color in sufficient quantity to produce the shade required, which can only be determined by experiment. The above-mentioned proportion of gum substitute may be varied to make the resist thicker or thinner to suit the printing as well as the proportion of the acetate.

After the aniline color is applied to the cloth it should be dried. It is then subjected to the action of steam under pressure in a steam-box or continuous steamer to develop the aniline-black and fix the pigment colors of the resist pattern, if they are used. After steaming, soap and wash in the usual way and the process is completed.

If the above-described resist is to be used as a discharge, it is to be printed on the aniline-black ground in the desired pattern after drying, and in this case the drying had best be conducted on the steam-cans until the cloth is in a moist state and then completed in an atmosphere of about 50° Fahrenheit, as described in another application I have filed contemporaneously herewith. It will be found that the aniline color will not oxidize rapidly enough to prevent the discharge from acting effectively and producing the required pattern in white or colors, as the case may be, upon the aniline-black ground, and after drying the cloth with the aniline color thereon it may be kept for several days in a cool atmos-

phere before the discharge is printed thereon, so perfectly is the oxidation of the aniline-black retarded by its composition as described. The treatment of the cloth after the discharge is printed thereon and it is again dried is the same as above described for the resist.

The oxidation of my aniline-black rapidly by the high heat of the steam under pressure develops it so rapidly around the resist or discharge pattern that the action of the alkali of the latter cannot have any effect in or around the outline of its pattern upon the shade or conformation of it, and also prevents the formation of free acid, which affects the pigment colors and the alkali of the discharge or resist pattern in a large degree, impairing their brightness and tone, as is the case if moisture and comparatively slow aging were employed to oxidize ordinary aniline-black colors. The patterns therefore appear upon the aniline-black ground, especially in whites, with a certainty and sharpness of outline which cannot be surpassed in clearness and boldness.

If neither a resist or discharge pattern is printed upon the cloth, the aniline-black will cover the same and form a plain black, and in this case as well as the others it will be found that the process or heat of the steam under pressure has not tendered the goods, even when so thoroughly saturated with the color as to develop on both sides alike, and I am therefore enabled to employ this fast steam aniline-black color for many purposes where it has not been heretofore successfully and certainly employed—such as yarns, plain cloths and umbrella-covers, &c., where the strength of the goods and durability of the color are of the highest importance.

What I claim as new and of my invention is—

1. The aniline-black color formed of ferro-cyanide of soda, chlorate of potash, and aniline salts prepared for use in such a manner as to be free from the presence of hydrochloric acid, substantially as set forth—that is to say, with the ferro-cyanide in amount sufficient to take up the aniline and prevent the formation of chlorate of aniline in injurious quantity in the color, substantially as described.

2. The aniline-black color formed of ferro-cyanide of soda, chlorate of potash, and aniline salts prepared for use in such a manner as to be free from the presence of hydrochloric acid, substantially as set forth—that is to say, with the ferro-cyanide in quantity sufficient to take up the aniline and the chlorate in quantity not less than thirty-five per cent. of that of the aniline, substantially as described.

JOHN BRACEWELL.

Witnesses:

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