UNITED STATES PATENT OFFICE.

EWALD HÖLKEN, OF BARMEN, GERMANY.

PROCESS OF MORDANTING.

SPECIFICATION forming part of Letters Patent No. 647,493, dated April 17, 1900.

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To all whom it may concern:

Be it known that I, EWALD HÖLKEN, a subject of the Emperor of Germany, residing at Barmen, in the Province of Rhenish Prussia, Germany, have invented certain new and useful Improvements in Black Dyeing; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to improvements in the process in dyeing with what is known as "vidal black" and equivalent sulfur coloring-matters. It is known that the substantive sulfur dyeing materials known as "black vidal," "noir vidal," "sulfur-black," "cachou de Laval," and others require after they have gone through the dyeing-bath a treatment with oxidizing means in a more or less hot bath. Some inventors prescribe baths of 40° to 50° Celsius—104° to 122° Fahrenheit—containing five to ten per cent. chromate of potash and five to ten per cent. sulfuric acid of 60° Baumé of the weight of the dyed goods. Others, again, recommend treating with three per cent. cupric sulfate and three per cent. acetic acid or with two per cent. chromate of potash and three per cent. acetic acid, two per cent. chromate of potash, and two per cent. cupric sulfate and three per cent acetic acid.

The goods dyed black by sulfur coloring-matters and such of the same group and treated afterward with acids and chromate of potash are not durable in washing, for when treated with soap the white fibers of goods treated at the same time get blue, and especially so when the stuffs thus treated are exposed to hot steam.

Goods treated with cupric sulfate, chromate of potash, and acetic acid, or with cupric sulfate and acetic acid combined, give only little color to white fibers combined with them. They "bleed" only little, as the technical term is; but they are subject to this disadvantage when stuffs or yarns dyed black by this means are mixed with white wool, as is the case in piece goods.

Now it is known that cotton yarns dyed black are very much used together with half-woolen and half-silk goods, and it is required that in such goods when dyed in pieces the wool or the silk shall in no way be influenced by the cotton, and the best durable black in this respect was considered hitherto the so-called "oxidation-black" and "one-bath anilin black," though they do not so far answer the requirements in the desired degree. These two black dyes give to the wool in the sulfuric bath a nasty violet tint, which shows itself the more the longer the stuff is exposed to the hot bath. They get greenish gradually, and both qualities make it difficult to produce tints coinciding exactly with the sample-pieces of wool or silk. Besides this, small particles of black dye precipitate from the black cotton, which soil the wool and spoil its brilliancy.

The colors produced by sulfur-black dyes are excellently qualified to supersede the anilin-black nearly exclusively used hitherto. Now though yarns treated with chromate of potash, cupric sulfate, and acetic acid afterward, or with cupric sulfate and acetic acid alone, do not spoil the woolen fibers, they have the other disadvantage that when the goods are steamed the copper salt contained in those black yarns combines itself with the sulfur contained therein, settling as a yellow-brownish color in the wool, which cannot be destroyed and makes it impossible to dye the wool in light brilliant colors. A similar effect is produced by the salts of other metals, the combinations of which with sulfur form black precipitations.

The novelty of my process consists in substituting therefor such metallic salts as form white combinations with sulfur, and consequently cannot discolor the wool. Experiments have proved that I attain this object in a most satisfactory degree by using salts of zinc for the after treatment of sulfur-blacks, and especially sulfurous hydrochloric and acetic salts of zinc.

The manner in which I proceed is shown in the following example:

The yarns dyed black are placed in a bath of 40° to 50° centigrade, to which are added four to six per cent. zinc sulfate, two to three per cent. chromate of potash, and two to three per cent. sulfuric acid (60° Baumé) of the weight of the goods. Other organic and inorganic acids may be used. The effect of this bath

upon the color, which up to this treatment had a greenish appearance, is as follows: The zinc sulfate fixes the color in the moment of the plunging of the goods into the bath, so that the yellow color of the bath is not altered in the least, and therefore the bath is held free of any impurity, whereas in other baths where no zinc sulfate is used the liquid takes a nasty greenish color. At the same time with the fixing of the dye a certain reaction of the chromic acid through the zinc chlorid shows itself, and by gradually raising the temperature of the bath the oxidation becomes more energetic and it is completed at the boiling heat. This is shown by the fact that the bath has now got quite clear without any yellowish or greenish tint. Chromic acid cannot be traced any more in the bath by the usual agencies. When chromic acid alone is used, nearly half of it remains in the bath. The more chromic acid is used, which must be regulated by the shade of the color required, the more full and effective is the color. I always give zinc chlorid in excess in order to attain the most perfect brilliancy. This excess of muriate of zinc can be easily washed out in the water-bath. With light black I only fix the color in a warmed bath of zinc chlorid, and I wash out afterward. I add to the zinc chlorid so much sulfuric acid that alkalies which may have remained in the goods will be neutralized. Cotton yarn dyed black with substantive sulfur dyes treated afterward in this manner is excellently fit for being used with half-woolen goods which are to be dyed in pieces in various colors, as well as for black goods. The color of the cotton will stand the most severe treatment, as hot washing, washing out the weaver's glue in the hot soap-bath, cleaning the wool in the ammoniacal bath, treating in high-pressure steam, the singeing and the finishing, and dyeing in the sulfuric bath, without in the least influencing the wool and without loosing itself of its fulness. The wool remains quite white.

Zinc chlorid has not been used hitherto in combination with chromate of potash and acids for the after treatment of goods or vegetable fibers, yarns, or woven goods dyed with substantive sulfuric dyes, and therefore

I claim as my invention—

1. The process of treating goods dyed in black by sulfur substantive dyes, consisting in the following steps; first, immersing the goods in a warmed bath of zinc sulfate, and afterward washing out said goods, substantially as and for the purpose set forth.

2. The process of treating goods dyed black by sulfur substantive dyes, consisting in treating the goods with zinc sulfate chromate of potash and chromic acid substantially as set forth.

3. The process of treating goods dyed in black by sulfur substantive dyes, consisting in the following steps: first immersing the goods in a warmed bath containing zinc sulfate chromate of potash and chromic acid; secondly, raising the temperature of said bath to the boiling-point, and thirdly, washing out the excess of zinc chlorid, substantially as and for the purpose set forth.

4. The process of treating goods of vegetable fiber dyed in black by "vidal black" or similar substantive dyes consisting in the following steps: first, adding to an aqueous bath from four to six per cent. of zinc sulfate, from two to three per cent. of chromate of potash, and from two to three per cent. of sulfuric acid (60° Baumé) at a temperature of 40° to 50° centigrade and forming zinc sulfate and chromic acid from the reactions of said ingredients while leaving a portion of the said chromate uncombined; secondly, immersing the goods in the bath thus constituted; thirdly, gradually raising the temperature of the bath to boiling heat to complete the oxidation and remove the chromic acid; fourthly, washing out any residual uncombined zinc sulfate, substantially as set forth.

In testimony whereof I have affixed my signature in presence of two witnesses.

EWALD HÖLKEN.

Witnesses:
Q. E. JOHN,
OTTO KÖEING.