## UNITED STATES PATENT OFFICE.

FRIEDRICH BAYER, OF ELBERFELD, GERMANY, ASSIGNOR TO FARBENFAB-RIKEN, VORMALS FR. BAYER & CO., OF SAME PLACE.

## PROCESS OF FIXING AZO DYES.

SPECIFICATION forming part of Letters Patent No. 418,153, dated December 31, 1889.

Application filed June 11, 1889. Serial No. 313,926. (No specimens.)

To all whom it may concern:

Be it known that I, FRIEDRICH BAYER, a subject of the King of Prussia and Emperor of Germany, residing at Elberfeld, in the Empire of Germany, director of and assignor to the Farbenfabriken, vormals Fr. Bayer & Co., have invented a new and useful Improvement in Dyeing and Printing Animal and Vegetable Fibers, of which I give in the 10 following a clear and exact description.

My invention relates to the improvement in dyeing and printing animal and vegetable fibers with those coloring-matters which possess the characteristic property of dyeing unmordanted cotton in an alkaline soap bath. Till now these dye-stuffs, which are also known in commerce under the names of "substantive cotton coloring-matters," could not be fixed fast enough for certain purposes, and were 20 likewise unfit for printing. These disadvantages are removed by my invention. I have found that they have the property of forming with the salts of metals compounds which in part are very permanent. I understand here 25 under substantive coloring-matters the azo colors derived from the tetrazo compounds of paradiamines. For example—benzidine, diamidophenyltolyle, tolidine, diamidodi-phenol ether, diamidostilbene and the sulpho 30 and carbonic acids thereof, paraphenylendiamine, naphthylendiamine diamidocarbazole, or those resulting by the reaction of phosgen on coloring-matters derived from paraphenylendiamine. By boiling in a solution 35 of a metallic salt, goods which have been dyed or printed in the usual way with the above characterized dye-stuffs the metals become fixed by the coloring-matter in the form of a fixed lac. The results thus obtained are nat-40 urally different according to the nature of the solution of the salts and the coloring-matters employed. However, in all cases a lac is formed which is fast to boiling water and to milling. In certain cases the metallic salts 45 also have the effect of changing the shade or color of the dye. Salts of iron, for example, make it redder. Other metals, such as zinc,

have no effect whatever on the shade of color. A remarkable result is obtained when salts 50 of copper are employed with coloring-matters

of diamidodiphenol ethers. These salts form with these coloring-matters a new compound having little similarity to the original shade. So, for example, benzo-azurine and benzo-azurine 3 G will be changed into a beautiful green- 55 ish blue. Azo violet gives a red blue. The other substantive cotton coloring-matters, which, for example, are derived from benzidine, do not possess this property and do not act in the same way.

The zinc lacs are best suited for wool and silk, as it has no influence on the shade and resists very well the action of boiling water or milling. The zinc is employed in the form

of sulphate of zinc or vitriol.

Example—Woolen goods dyed in the usual way with deltapurpurine are boiled for a few minutes with five per cent of white vitriol corresponding to the dye employed. wool so treated is now perfectly fast to full- 70 ing and milling, and can be treated with boiling water without suffering. On cotton goods the direct dyeing coloring matters do not form with the metals in general such resistant lacs as in the case of animal fibers. Never- 75 theless combinations are formed which enable the process to be employed with considerable advantage in practice.

The lacs formed with sulphate of copper and nickel are considerably faster to soap, 80 and stand hot soaping at 40° centigrade, while dyes not so prepared are known to suffer even by cold soaping. In particular, cotton yarns and fabrics dyed with the blue coloring-matters derived from the diamidodi- 85 phenol ethers—such as benzo-azurine or azo violet—especially the benzo-azurine 3 G, are not only rendered faster to soap by boiling with blue vitriol, but also change their shade very essentially to green, lose the particular 90 and disagreeable property, which they possess, of turning red when exposed to heat, and are absolutely resistant to light.

The improved process can be employed in printing in the same way as in dyeing. Goods 95 which have been dyed with benzo-azurine and then boiled with sulphate of copper or blue vitriol cannot be dischanged in the usual way with salt of tin.

Having thus described my invention, what I 100

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

The process for printing and dyeing the substantive cotton coloring matters which possess the property of dyeing unmordanted cotton in an alkaline soap bath by boiling goods of animal or vegetable fibers which have been dyed or printed in the usual way with the substantive cotton coloring-matters

with a solution of a metallic salt, substan- 10 tially as described.

In testimony whereof I have signed my name in presence of two subscribing witnesses.

FRIED. BAYER.

Witnesses:

CARL DENSBERG, CARL HIRLSENBUSCH.