

UNITED STATES PATENT OFFICE.

WILHELM HERZBERG AND OSWALD SCHARFENBERG, OF BERLIN, GERMANY,
ASSIGNORS TO THE ACTIEN-GESELLSCHAFT FÜR ANILIN FABRIKATION,
OF SAME PLACE.

GREEN-BLUE DYE.

SPECIFICATION forming part of Letters Patent No. 647,834, dated April 17, 1900.

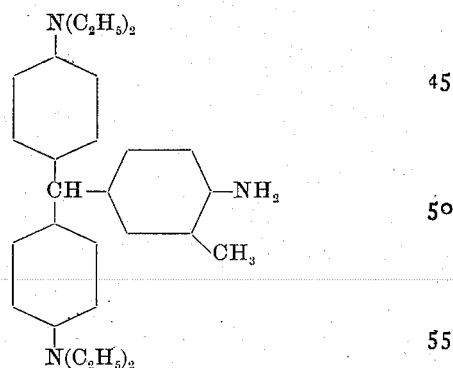
Application filed December 22, 1899. Serial No. 741,291. (No specimens.)

To all whom it may concern:

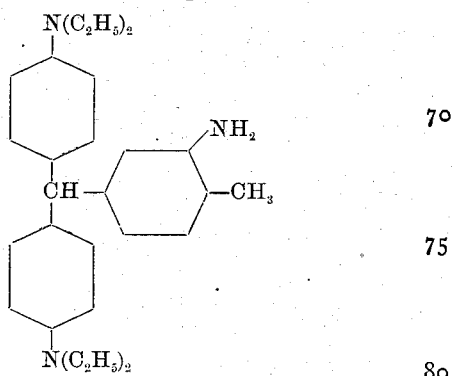
Be it known that we, WILHELM HERZBERG and OSWALD SCHARFENBERG, of Berlin, in the Kingdom of Prussia, German Empire, have invented new and useful Improvements in the Production of Green-Blue Dye; and we do hereby declare that the following is a full, clear, and exact description of the invention, which will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to the production of a green-blue dyestuff belonging to the triphenylmethane series and is based on the following observations:

We have made the discovery that ortho-toluidin when subjected to the condensation with tetraethyldiamidobenzhydrol in the presence of strong sulfuric acid as condensing agent yields a product which by its properties essentially differs from the leuco base obtained from the same components when the condensation is performed in diluted acid solutions. While the last-mentioned leuco compound yields on oxidation a blue-violet coloring-matter, the new leuco compound which we have prepared is transformed by oxidation into a green-blue dye. According to all observations on this subject hitherto published the condensations of tetraalkyldiamidobenzhydrols with amido compounds in diluted solutions unexceptionally take place in such manner that the CH group of the hydrol enters into para position to the amido group, provided that this position is free. (Compare German patent (expired) No. 27,032; *Nölting, Berichte der Deutschen Chemischen Gesellschaft*, XXII, page 554.) The leuco base formed in diluted solutions—for instance, from ortho-toluidin and tetraethyldiamidobenzhydrol—is therefore represented by the formula:

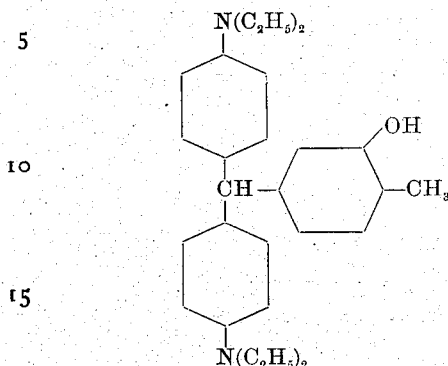


The difference between this condensation product and the new product obtained by us can only be due to the fact that under the influence of strong sulfuric acid the CH group of the hydrol has entered into another position to the amido group of the ortho-toluidin. According to our researches it appears most probable that the constitution of the new leuco base is the following:



that is to say, that the CH group has entered into meta position to the NH₂ group. We have further found that the new leuco base produced in the way described can easily be

diazotized and by boiling off the diazo solution obtained converted with very good yield into the corresponding oxyleuco base:



In carrying our researches further we have, moreover, discovered that this oxyleuco base is transformed by sulfonation and oxidation into a dyestuff which has been found to be a monosulfo-acid and which dyes wool and silk green-blue tints of great intensity. It is distinguished by its fastness to alkalis and its remarkable power of dyeing even shades.

To further illustrate our invention, we give the following directions:

1. *Production of tetraethyldiamidodiphenyl-meta-amido-para-tolylmethane.*—32.6 kilos of tetraethyldiamidobenzhydrol are dissolved in three hundred kilos of sulfuric acid monohydrate, and into the solution obtained 10.7 kilos of ortho-toluidin (respectively 15.6 kilos of ortho-toluidin sulfate) are introduced. By allowing the mixture to stand at a temperature of 20° the condensation is completed after twelve hours. The mass is thrown on ice, diluted with water, and neutralized by means of sodium carbonate, whereupon the leuco base separates in the form of a white-gray powder. It crystallizes from hot alcohol in the form of white leaflets, melting at 95° to 96°. It is slightly soluble in hot alcohol, benzene, and ether.

2. *Production of tetraethyldiamidodiphenyl-meta-oxy-para-tolyl-methane.*—A refrigerated solution of seven kilos of sodium nitrite in sixty liters of water is allowed to run slowly into a solution of 41.5 kilos of the above-described leuco base in three hundred liters of water and sixty kilos of concentrated sulfuric acid. The solution obtained is heated to 50° to 60° and maintained at this temperature until the diazo compound is totally decomposed. After refrigeration the oxyleuco base is precipitated in the shape of gray-white flakes by the addition of caustic-soda lye or sodium carbonate. It crystallizes from ligroin in the form of hard lustrous prisms, melting at 106° to 107°. It is slightly soluble in alcohol and ether, and hardly soluble in cold ligroin.

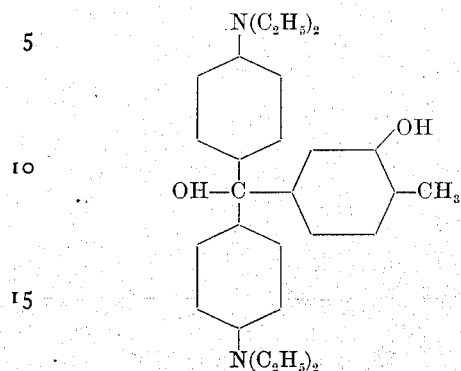
3. *Production of the dyestuff.*—41.6 kilos of the above-described oxyleuco base are dissolved in the cold in one hundred and sixty kilos of sulfuric acid monohydrate and twenty-five kilos of sulfuric acid containing sixty per cent. SO_3 . The mixture is allowed to stand at about 20° until a sample dissolves completely in sodium carbonate. The reaction product is then thrown on water and ice, and the free sulfuric acid is for its greatest part neutralized by means of lime. The acid solution is separated from the calcium sulfate by filtration and entirely neutralized with carbonate of soda. From the solution thus obtained the sodium salt of the leuco-sulfo-acid may be precipitated in the shape of a white powder by addition of common salt. It is, however, not necessary to isolate this sodium salt, the oxidation product being as well obtained from the leuco solution directly by oxidation. The free leucosulfo-acid is obtained in the shape of white flakes by adding to an aqueous solution of its sodium salt the theoretically-required quantity of acetic or mineral acid. It dissolves in an excess of these acids. From diluted solutions it crystallizes in almost colorless needles. The sulfo-acid forms a calcium salt which is almost insoluble in water. The oxyleuco-sulfonic acid thus produced is converted into the corresponding dyestuff by treatment with an oxidizing agent, as illustrated by the following example: 51.9 kilos of the sodium salt of the oxyleuco-sulfonic acid are dissolved into five hundred liters of water, and the theoretical quantity of sulfuric acid and peroxid of lead are added thereto. After filtering off the sulfate of lead the new dyestuff is precipitated from the solution obtained by means of common salt. The same dyestuff is obtained by first oxidizing the oxyleuco base prepared as above described and afterward sulfonating the coloring-matter formed by the oxidation.

The dyestuff forms small green leaflets of metallic luster, easily soluble in water with blue coloration and very soluble in cold alcohol. The blue aqueous solution turns yellow when an excess of mineral acid is added. On diluting this acid solution it assumes a green coloration. Sodium carbonate or ammonia do not effect any change of color even when the aqueous solution is heated with these agents. The solution of the dye remains unchanged when caustic-soda lye is added in the cold; but when boiled with the soda-lye it assumes a red-violet coloration. The new coloring-matter dyes wool and silk in acid-bath fine green-blue tints.

Having now described our invention and in what manner the same can be performed, what we claim as new is—

The green-blue dye belonging to the triphe-

nylmethane series being a salt of the monosulfonic acid of the product having probably the formula:



the sodium salt of this dye being easily solu-

ble in water or alcohol with blue coloration, the aqueous solution of said salt turning yellow on the addition of an excess of mineral acid and assuming a green coloration when this acid solution is diluted; the solution remaining unchanged when heated with sodium carbonate or ammonia, or when treated with caustic-soda lye in the cold, but assuming a red-violet solution when boiled with this latter agent; the new coloring-matter dyeing silk and wool green-blue tints.

In witness whereof we have hereunto signed our names, this 8th day of December, 1899, in the presence of two subscribing witnesses.

WILHELM HERZBERG.

OSWALD SCHARFENBERG.

Witnesses:

WOLDEMAR HAUPT,

HENRY HASPER.