

UNITED STATES PATENT OFFICE.

ROBERT E. SCHMIDT, OF ELBERFELD, GERMANY, ASSIGNOR TO THE
FARBENFABRIKEN, VORMALS FR. BAYER & CO., OF SAME PLACE.

ALIZARINHEXACYANIN.

SPECIFICATION forming part of Letters Patent No. 506,265, dated October 10, 1893.

Application filed May 11, 1892. Serial No. 432,611. (Specimens.) Patented in England March 12, 1892, No. 4,871.

To all whom it may concern:

Be it known that I, ROBERT E. SCHMIDT, doctor of philosophy and chemist, (assignor to the FARBENFABRIKEN, VORMALS FR. BAYER & Co., of Elberfeld,) a subject of the Emperor of Germany, residing at Elberfeld, Germany, have invented a new and useful Improvement in the Manufacture of Alizarin Derivatives, (for which the aforesaid FARBENFABRIKEN have already obtained Letters Patent in Eng-
land, No. 4,871, dated March 12, 1892,) of which the following is a clear and exact description.

I have described in the United States Letters Patent No. 446,893, dated February 24, 1891, the production of an alizarin derivative called "alizarin bordeaux" which I have obtained by oxidizing alizarin with a large excess of sulfuric anhydride in the form of a strong fuming sulfuric acid at a low temperature.

In the United States Letters Patent No. 446,892, dated February 24, 1891, I have described another valuable alizarin dye-stuff which is produced by oxidizing the aforesaid alizarin bordeaux in sulfuric acid solution with manganese dioxid. While the alizarin bordeaux is a tetraoxyanthraquinone the product resulting from alizarin bordeaux by further oxidation represents a pentaoxyanthraquinone. In order to express the constitution and the cyanine like character of this latter product I briefly term it "alizarin pentacyanin."

My new invention relates to the production of a new coloring-matter by further oxidizing the said alizarin pentacyanin a dye-stuff being thus formed which is a hexaoxyanthraquinone and which I briefly term "alizarin hexacyanin." It is different from the alizarin pentacyanin by its composition and properties, from the isomeric hexaoxyanthraquinone which I have described and claimed in a separate application and which I briefly term "hexaoxyanthraquinone" it chiefly differs by its dyeing properties. The production of this new coloring-matter called "alizarin hexacyanin" may be carried out in the following different ways: first, by oxidizing alizarin pentacyanin or alizarin bordeaux in sulfuric acid solution with manganese dioxid, arsenic

acid or other suitable oxidizing agents; secondly, by heating alizarin pentacyanin with concentrated sulfuric acid at higher temperatures the sulfuric acid effecting the oxidation of the employed alizarin pentacyanin; thirdly, by the oxidation of anthrapurpurin in sulfuric acid solution with manganese dioxid or other suitable oxidizing agents.

I have found that in the first two processes a mixture of alizarin hexacyanin and hexaoxyanthraquinone is produced while in the third process only alizarin hexacyanin is formed, as the first produced oxyanthrapurpurin (tetraoxyanthraquinone) which corresponds with anthrapurpurin in a like manner as purpurin does with alizarin, is totally changed into alizarin hexacyanin by the further action of the oxidizing agents employed.

In carrying out the preceding three processes practically I proceed as follows: Ten parts, by weight, of dry alizarin pentacyanin are dissolved in two hundred parts, by weight, of concentrated sulfuric acid of 66° Baumé and five parts, by weight, of finely pulverized manganese dioxid containing ninety per cent. of dioxid, are gradually added. In the first place the quinone of alizarin pentacyanin, a so called anthradiquinone, is formed which may be recognized when a portion of the resulting mixture, dissolved in concentrated sulfuric acid, shows no more distinct absorption bands when looked at in the spectroscope. The quinone of alizarin pentacyanin, then, is converted into the quinone of alizarin hexacyanin by the further action of the manganese dioxid, employing advantageously a somewhat higher temperature. Therefore it is most practical to heat the mixture under continual stirring at a temperature of about 50° centigrade until a test portion after pouring into water and boiling with acid sodium sulfite forms a precipitate the solution of which in concentrated sulfuric acid shows no more the absorption bands of alizarin pentacyanin. The resulting mixture then is poured into two thousand parts, by weight, of water adding ten parts, by weight, of an aqueous acid sodium sulfite solution of 34° Baumé. After heating to the boiling point

the coloring-matter separating is filtered off and washed out. The latter is redissolved in the necessary quantity of soda-lye and the alkaline solution after having been filtered 5 is decomposed by the addition of acids. The product precipitated is a mixture of alizarin hexacyanin and hexaoxyanthraquinone, as above mentioned. In order to remove the latter, the mixture is crystallized at first out 10 of nitrobenzene, then repeatedly out of alcohol, in which the hexaoxyanthraquinone is more difficultly soluble than alizarin hexacyanin. A second and best method of separating the two coloring-matters of the above 15 mixture is to be carried out by heating the mixture with sodium acetate and acetic acid anhydrid and boiling the resulting mixture of the two isomeric hexa-acetyl-compounds with acetone by which the hexa-acetyl deriv- 20 ative of hexaoxyanthraquinone is not dissolved while that of alizarin hexacyanin easily dissolves in the said solvent. By saponifying the acetyl compounds thus separated the alizarin hexacyanin and hexaoxyanthra- 25 quinone are obtained in a pure state.

As alizarin pentacyanin is produced by oxidizing alizarin bordeaux, it is not necessary to start from alizarin pentacyanin but alizarin bordeaux may be employed without 30 isolating the alizarin pentacyanin produced as an intermediate product.

The following is an example for the conversion of alizarin bordeaux into alizarin hexacyanin: Ten parts, by weight, of dry alizarin 35 bordeaux are dissolved in two hundred parts, by weight, of concentrated sulfuric acid at 66° Baumé and fifteen parts, by weight, of finely pulverized manganese dioxid (containing ninety per cent. of dioxid) are gradually 40 introduced, the temperature being kept at from 50° to 55° centigrade. The gradual conversion of alizarin bordeaux into alizarin pentacyanin and alizarin hexacyanin is to be recognized very distinctly by the usual spectroscopic examination. When the spectrum 45 of the pentacyanin has totally disappeared the sulfuric acid liquid is treated in the same manner as described in the preceding example.

In order to oxidize alizarin bordeaux in sulfuric acid solution by means of arsenic acid a higher temperature for example from 140° to 160° centigrade is necessary. The alizarin pentacyanin formed at first in this 55 operation seems to be immediately converted into alizarin hexacyanin and hexaoxyanthraquinone, as in the spectroscopic examination of the oxidation products the alizarin pentacyanin is always to be recognized only in very 60 small traces.

The following may be given as an example for the preparation of alizarin hexacyanin by oxidizing alizarin bordeaux by means of arsenic acid: A mixture of ten parts, by weight, 65 of alizarin bordeaux, two hundred parts, by weight, of sulfuric acid at 66° Baumé and fif-

teen parts, by weight, of dry arsenic acid are heated for about six hours at a temperature from 140° to 150° centigrade and the resulting mixture then is poured into water. By 70 filtering off, redissolving in alkali and precipitating again with acids, separating the two products formed in the manner before described the alizarin hexacyanin dye-stuff is isolated. 75

Of course, on starting from alizarin pentacyanin in the last example a smaller quantity of arsenic acid is necessary for effecting the oxidation of alizarin pentacyanin into alizarin hexacyanin. At the high tempera- 80 ture employed in this example as well as in the following quinones are not formed as I have found the mixture contains the coloring matters and not the quinones thereof.

In order to produce alizarin hexacyanin by 85 treating alizarin pentacyanin with concentrated sulfuric acid at higher temperatures I proceed as follows: Ten parts, by weight, of alizarin pentacyanin and two hundred parts, by weight, of sulfuric acid at 66° Baumé are 90 heated at 190° centigrade until a sample of the mixture diluted with sulfuric acid shows no more the spectrum of alizarin pentacyanin. When the latter has been found to be totally 95 converted the whole liquid is poured into water and the coloring matter separated by filtering off, washing out and isolated in the manner above described.

Anthrapurpurin is converted into pure alizarin hexacyanin by an energetic oxidation 100 with the aid of manganese dioxid. In the first place there is formed oxyanthrapurpurin which is a coloring-matter dyeing a yellowish-red on cotton mordanted with alumina salts, but possesses only an inferior value for dye- 105 ing purposes. By the further oxidation the oxyanthrapurpurin is transformed into the quinone of alizarin hexacyanin and this quinone, is then converted into the cyanin (alizarin hexacyanin) by a subsequent treat- 110 ment with reducing agents employing most practically sulfurous acid. The following example may illustrate how this operation is to be carried out: A pulverized mixture con- 115 taining ten parts, by weight, of anthrapurpurin and nineteen parts, by weight, of manganese dioxid (ninety per cent.) is introduced with constant agitation into three hundred parts, by weight, of sulfuric acid at 66° 120 Baumé taking care that the temperature does not rise above 35° centigrade. After the whole manganese dioxid has been added, the mixture is allowed to stand for half an hour. Then it is poured into three thousand 125 parts, by weight, of water mixed with ten parts, by weight, of an aqueous solution of sodium bisulfite at 35° Baumé. The liquid is heated to the boiling point and the coloring-matter separated is filtered off, washed out and purified by redissolving, &c., in the well 130 known manner.

I have further found that in general in or-

der to separate pure alizarin hexacyanin from other oxyanthraquinones especially in case the former be in excess the best method is the following: The mixture is dissolved in twenty times its weight of concentrated sulfuric acid and after heating to 100° centigrade water is gradually added to the cooled solution. In this manner the hexacyanine is precipitated at first and in a pure state as the other oxyanthraquinones, remain dissolved in the diluted sulfuric acid solution. The alizarin hexacyanin can readily be isolated by filtration.

My new product thus obtained and called "alizarin hexacyanin" is insoluble in water and very moderately soluble in alcohol with dark rose-red color and in glacial acetic acid with a more yellowish-red color both solutions showing a yellowish-brown fluorescence. Out of alcohol or glacial acetic acid it separates in dark brilliant crystals. It is easily soluble in boiling nitrobenzene and very easily in pyridin. When its alkaline solutions are decomposed by adding acids or on pouring its solution in concentrated sulfuric acid into water it separates in reddish-brown flakes which after filtering off yield a dark brown paste that is most fit for dyeing and printing purposes. It dissolves in sodium carbonate with bluish-violet color, in ammonia at first with dull brownish-violet color which gradually changes into a pure and beautiful blue when the solution is allowed to stand in open vessels. By soda-lye it is dissolved with greenish-blue color and out of this solution when in contact with the atmospheric air dark violet flakes separate which I have found are the sodium salt of the quinone of alizarin hexacyanin. Its solution in concentrated sulfuric acid possesses a bluish color and shows when looked at with the spectroscope two characteristic absorption bands namely: the one in the red part and the other between the yellow and green part of the spectrum. This sulfuric solution, however, assumes a color more greenish when it is allowed to stand for a longer time and then shows in the spectroscopic research one absorption band in the red part of the spectrum considerably stronger while the other between the green and yellowish part of the spectrum has become smaller. By slowly adding water to the sulfuric solution of the dye-stuff the color at first changes into violet, then red and at last the alizarin hexacyanin separates in brownish-red flakes.

The alizarin hexacyanin chiefly differs from the hexaoxyanthraquinone described by me in a separate specification by the following properties: Alizarin hexacyanin dissolves in a solution of sodium carbonate with bluish-violet, in soda-lye with greenish-blue color, dark violet flakes being separated out of such solution in soda-lye after some time in the air, in ammonia with dull brownish-violet color,

which changes into blue in the air, and in pure concentrated sulfuric acid with blue color which turns green by standing and on adding water to such sulfuric acid solution at first into violet, then into red, brownish-red flakes being separated after some time. Hexaoxyanthraquinone dissolves in a solution of sodium carbonate with bluish-red, in soda-lye with violet color which gradually turns into blue in the air blue flakes being further separated after some time, in ammonia liquid with bluish-red color which changes into violet in the air, in pure concentrated sulfuric acid with bluish-violet color which turns into yellowish-red on adding water, yellowish-brown flakes being separated after some time. The said alizarin derivatives further differ by the absorption spectra of their sulfuric acid solutions. Alizarin hexacyanin displays two strong absorption bands, the one in the red part and the other in the green part of the spectrum, while hexaoxyanthraquinone shows one strong absorption band in the orange part and a slighter one in the yellowish-green part of the spectrum.

The shades produced by alizarin hexacyanin on wool mordanted with chromium or alumina salts are in general more greenish than those obtained by employing hexaoxyanthraquinone. It produces on wool mordanted with alumina salts violet, on wool mordanted with chromium salts blue shades both being more greenish than those resulting from the alizarin pentacyanin and hexaoxyanthraquinone which I have described in separate specifications.

By analyzing the crystalized product I have found it to be a hexaoxyanthraquinone of the formula $C_{14}H_2O_2(OH)_6$ isomeric with the hexaoxyanthraquinone obtained by me and described in a separate specification, Serial No. 412,304, filed November 18, 1891.

Having thus described my invention, what I claim as new, and desire to secure by Letters Patent, is—

1. The process of producing a new alizarin dye stuff by oxidizing alizarin pentacyanin or alizarin bordeaux, substantially as described.

2. The new dye herein described, insoluble in water, moderately soluble in alcohol and glacial acetic acid with yellowish-brown fluorescence, crystallizing from these solvents in dark brilliant crystals; easily soluble in boiling nitro benzol, and in pyridin; soluble in aqueous ammonia with a dull brownish color, which changes on exposure to air to a pure blue; soluble in alkali carbonates and caustic alkalies, from which solutions acids precipitate the dye stuff in reddish-brown flakes, which, after filtering and washing, are a very suitable paste for use in the arts, producing violet shades with aluminum mordants and blue shades with chrome mordants, forming with concentrated sulfuric acid a bluish solution which shows an absorption band in the

red and one between the yellow and green
part of the spectrum, and assumes a more
greenish color on standing for a long time, at
the same time enlarging the absorption band
5 in the red and diminishing the one between
the yellow and green part of the spectrum,
having the qualities substantially as set forth.

In testimony whereof I have signed my
name in the presence of two subscribing wit-
nesses.

ROBERT E. SCHMIDT.

Witnesses:

WM. ESSENWEIN,
RUDOLPH FRIEKE.