

UNITED STATES PATENT OFFICE.

HEINRICH CARO, OF MANNHEIM, GRAND DUCHY OF BADEN, AND CHARLES GRAEBE AND CHARLES LIEBERMANN, OF BERLIN, PRUSSIA.

IMPROVEMENT IN THE PREPARATION OF COLORING MATTERS FROM ANTHRACENE.

Specification forming part of Letters Patent No. **153,536**, dated July 28, 1874; application filed January 26, 1870.

To all whom it may concern:

Be it known that we, HEINRICH CARO, of Mannheim, in the Grand Duchy of Baden, and CHARLES GRAEBE and CHARLES LIEBERMANN, both of Berlin, in the Kingdom of Prussia, have invented certain new and useful Improvements in Preparing Coloring Matters, of which the following is a specification:

This invention relates to improvements on an invention described in Letters Patent of the United States granted to Charles Liebermann and Charles Graebe for improvements in preparing coloring matters, dated the 5th day of October, 1869, No. 95,465, in which the preparation of artificial alizarine is based upon the action of caustic alkalies upon bibrom-anthrakinon or bichlo-ranthrakinon. We have now discovered that a similar result may be obtained by substituting sulphuric acid for bromine or chlorine in the above process. We thus obtain the sulpho-acids of anthrakinon, which, by being dissolved in and heated with an excess of caustic alkali, are converted into alizarine. This invention relates to improvements in the production of coloring matters, and more especially to improvements in the methods of producing what is known as artificial alizarine from anthracene—a method of producing which was described in the above-named Letters Patent, and consisted in the production of artificial alizarine by converting anthracene into either bibrom-anthrakinon or bichlo-ranthrakinon, and then acting upon the same by means of an alkali, and precipitating the alizarine contained in the alkaline solution by means of an acid.

In the complete specification of the aforesaid Letters Patent granted to Charles Liebermann and Charles Graebe two different series of processes are described for obtaining the brominated or chlorinated derivatives of anthrakinon.

In the first of these processes the anthracene is submitted to the action of oxidizing agents, as is well understood, and the oxidized anthracene or anthrakinon is then treated with bromine or chlorine.

In the second of these processes the anthracene is first treated with bromine or chlorine, and subsequently submitted to an oxidizing

process, in order that the desired compounds, *videlicet*, bibrom-anthrakinon or bichlo-ranthrakinon, may be obtained.

In an analogous manner we now employ sulphuric acid as a substitute for the bromine or chlorine employed in the processes above referred to, and we thus obtain the sulphuric-acid derivatives of anthrakinon, which we call "the sulpho-acids of anthrakinon."

Our invention is carried into effect by means of either of the two processes, which we will proceed to describe.

In the one process we proceed as follows: We take about one part, by weight, of anthrakinon, and about three parts, by weight, of sulphuric acid of about the specific gravity of 1.840, and introduce the same into a retort, which may be made of glass, or of porcelain, or of other material not easily acted upon by sulphuric acid, and the contents are then to be heated up to about 260° centigrade, and the temperature is maintained until the mixture is found no longer to contain any appreciable quantity of unaltered anthrakinon. The completion of this desired operation may be ascertained or tested by withdrawing a small portion of the product from time to time, and continuing the operation at the high temperature until such product, upon being diluted with water, is found to form a substantially perfect solution, thereby indicating that the anthrakinon has become either entirely or in greater part converted into the desired product. The results of this operation are then allowed to cool and are diluted with water. We then add carbonate of lime in order to neutralize and remove the excess of sulphuric acid contained in the solution. The mixture is then filtered, and to the filtrate carbonate of potash or carbonate of soda, by preference in solution, is to be added until carbonate of lime is no longer precipitated. The mixture is then filtered and the clear solution is evaporated to dryness, by which means the potash or soda-salts of what we call the "sulpho-acids of anthrakinon" are obtained, and which are to be treated in the following manner: We take about one part, by weight, of this product, and from two to three parts, by weight, of solid caustic soda or potash. Water may

be added or not, but by preference we add as much water as is necessary to dissolve the alkali. After admixture we heat the whole in a suitable vessel, and the heating operation is continued at a temperature of from about 180° to about 260° centigrade for about one hour, or until a portion of the mixture is found, upon withdrawing and testing it, to give a solution in water, which, being acidulated with an acid—for example, sulphuric acid—will give a copious precipitate of the coloring matters. The heating operation having been found to have been continued for a sufficient time, the resulting products are then dissolved in water, and we either filter or decant the solution of the same, from which we precipitate the coloring matters or artificial alizarine by means of a mineral or organic acid, such, for example, as sulphuric or acetic acid. The precipitated coloring matters thus obtained are collected on a filter or otherwise, and, after having been washed, may be employed for the purposes of dyeing and printing, either in the same way as preparations of madder are now used or otherwise.

In carrying out our other process we proceed as follows: We take about one part, by weight, of anthracene, and about four parts, by weight, of sulphuric acid of specific gravity of about 1.848, and the mixture, being contained in a suitable vessel, is heated to a temperature of about 100° centigrade, at which temperature it is to be maintained for the space of about three hours. The temperature is then to be raised to about 150° centigrade, which temperature is to be maintained for about an hour, or until a small portion of the product, when submitted to the subsequent processes hereinafter described, is found to produce the desired coloring matters. We then allow the result obtained by this operation to cool and dilute it with water, by preference in the proportion of about three times its weight. To the solution thus obtained we add, for every part of anthracene, by weight, which had been employed in the previous operation, about from two to three parts, by weight, of peroxide of manganese, preferring to employ an excess, and we boil the whole strongly for some time; and, in order to fully insure the desired degree of oxidation, the mixture may be subsequently concentrated, and, by preference, be evaporated to dryness, and the heat be continued until a small portion of the oxidized product, when submitted to the subsequent processes hereinafter described, will produce the desired coloring matters. We then neutralize and remove the sulphuric acid contained in this mixture, and at the same time precipitate any oxide of manganese which may be held in solution, by adding an excess of caustic lime, which we use, by preference, in the form of milk of lime, and we add the same until the mixture has an alkaline reaction. We then filter and add to the filtrate carbonate of potash or soda until there is no further precipitation of carbonate of lime. The solu-

tion is then filtered and evaporated to dryness; and we thus obtain the potash or soda-salts of what we call "the sulpho-acids of anthrakinon."

In effecting the conversion of the oxidized products thus obtained into coloring matters, or into what we call "artificial alizarine," we proceed as follows: We take one part, by weight, of this product, and from two to three parts, by weight, of solid caustic soda or potash; and water may be added or not; but, by preference, we add as much water as is necessary to dissolve the alkali. After admixture we heat the whole in a suitable vessel, and continue the heating operation, at a temperature from about 180° to about 260° centigrade, for about one hour, or until a portion of the mixture is found to give solution in water, which, upon acidulation with an acid—for example, sulphuric acid—is found to give a copious precipitate of the coloring matters. The heating operation having been found to have been continued for a sufficient time, we then dissolve the product in water, and either filter or decant the solution of the same, from which we precipitate the coloring matters or artificial alizarine by means of a mineral or organic acid—such, for example, as sulphuric or acetic acid. The precipitated coloring matters thus obtained are collected on a filter or otherwise, and, after having been washed, may be employed for the purposes of dyeing and printing, either in the same way as preparations of madder are now used or otherwise.

Instead of acting upon anthracene by means of sulphuric acid of the density before mentioned, fuming sulphuric acid may be employed; but we prefer to use the ordinary acid, as before described.

In order to effect the process of oxidation before referred to, other oxidizing agents may be used in place of the peroxide of manganese before mentioned—such, for example, as peroxide of lead; or chromic, nitric, or other acids capable of effecting the desired oxidation may be employed. If the oxidizing agent be a soluble one—such, for instance, as chromic acid—any excess of the oxidizing agent that may have been employed should be removed or reduced before proceeding with the subsequent operation. Thus, for example, had chromic acid been used in excess, sulphurous acid may be passed through the product before adding the lime. In the case of the employment of nitric acid the oxidized mixture should be heated until the greater proportion of the nitric acid has been evaporated, and until the sulphuric acid has become so concentrated that it commences to volatilize.

Although we have mentioned the employment of carbonate of lime and of caustic lime for the purpose of effecting the neutralization of the sulphuric acid existing in the solution of the products obtained from the treatment of anthrakinon, and from anthracene, as hereinbefore described, it will be understood that other bases which will neutralize the acid, and

which will not in any way be injurious in any of the subsequent processes, may be substituted for the same.

Having now described our invention, and methods we employ in carrying it into effect, we claim—

1. The manufacture of coloring matters by submitting anthrakinon to the action of sulphuric acid, so as to obtain soluble compounds, which we have called "sulpho-acids of anthrakinon," treating the products of such operation with an alkali, and precipitating the coloring matters therefrom by means of an acid, as herein described.

2. The manufacture of coloring matters by submitting anthracene to the action of sulphuric acid, oxidizing the product thereby obtained, heating such oxidized product with an

alkali, and subsequently precipitating the coloring matters therefrom by means of an acid, as herein described.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

HEINRICH CARO.

CHARLES GRAEBE.

CHARLES LIEBERMANN.

Witnesses to the signature of HEINRICH CARO and CHARLES GRAEBE:

J. HENRY JOHNSON,

THOS. A. BYRNE,

Clerk to J. Henry Johnson.

Witnesses to the signature of CHARLES LIEBERMANN:

H. KREISMANN,

HERMAN ZUNGE.