

UNITED STATES PATENT OFFICE.

HEINRICH CARO, OF MANNHEIM, GERMANY.

IMPROVEMENT IN OBTAINING COLORING MATTERS SUITABLE FOR DYEING AND PRINTING.

Specification forming part of Letters Patent No. **186,032**, dated January 9, 1877; application filed October 2, 1876.

To all whom it may concern:

Be it known that I, HEINRICH CARO, of Mannheim, in the Empire of Germany, chemist to the Badische Anilin and Soda Fabrik of Mannheim aforesaid, Grand Duchy of Baden, have invented Improvements in Obtaining Coloring Matters Suitable for Dyeing and Printing, of which the following is a specification:

This invention relates to improvements in preparing coloring matters suitable for dyeing and printing from pure or commercial alizarine.

Alizarine, as is well known to chemists, is easily acted upon by nitric acid, the result being either complete destruction of its molecule or the production of an unstable nitro compound, which, by the action of water or alkalies, is rapidly converted into nitro-oxy-alizarine—a coloring matter possessing properties similar to purpurine.

It is only by a circuitous manner—namely, by first converting alizarine into its diacetyl compound, and subsequently treating the same with nitric acid, or by submitting textile fabrics dyed or printed with alizarine-reds to the action of nitrous vapors or of nitric acid, and afterward extracting the coloring matter which has undergone alteration therefrom—that coloring matters or nitro compounds of alizarine have been obtained, which differ from the above-mentioned unstable product by being capable of imparting a permanent orange-red dye to alumina mordants.

According to my present invention, similar coloring matter or matters, which I propose to term “alizarine-orange,” may be produced in a direct manner from alizarine itself, such alizarine being employed either in its pure state or in the commercial condition in which the various preparations from madder or the artificial alizarines synthetically prepared from coal-tar are delivered to the trade, and which products contain, besides alizarine, more or less other compounds, such as isopurpurine, anthrapurpurine, or purpurine. All such preparations I hereafter call “commercial alizarine.” The said pure or commercial alizarine may, according to my invention, be converted into alizarine-orange by the action of nitrous hyponitric or nitric acids, such acids

being used for this purpose either in their free state, singly or mixed with one another, or such as result from the mutual decomposition of any saline compound of the same with any other acid or acids, mineral or organic, which are capable of liberating the said nitrogen acids from their saline compounds.

This invention may be carried out in the following manner: Pure or commercial alizarine, preferably dry and in a fine state of division, is spread out in thin layers, and exposed in a closed chamber or otherwise to the action of nitrous hyponitric or nitric acids, such acids being employed in a gaseous condition, and either singly or mixed with one another; but I generally prefer their gaseous mixture, practically known as “nitrous fumes,” resulting as a by-product from various processes in which nitric acid is employed as an oxidizing-agent. I then allow the action to proceed at the ordinary atmospheric temperature, or at an elevated temperature, until the desired change has been accomplished.

This result may be ascertained by withdrawing a sample of the product from time to time, and by testing it for the presence of unaltered alizarine therein, by any of the well-known methods generally used for that purpose. If, for instance, tested with caustic alkalies, the purple solution of the alkaline alizarates is no longer obtainable, the operation may be considered at an end, and the alizarine-orange should be withdrawn from the further action of the nitrogen acids.

The same coloring matter may also be obtained by mixing pure or commercial alizarine with, or dissolving it in, a suitable solvent, which solvent is not easily acted on by the nitrogen acids, such as ether, glacial acetic acid, bisulphide of carbon, benzole, petroleum, nitro-benzole, or similar substances, or mixtures of two or more of them; and the mixture or solutions thus obtained I heat with nitrous acid, hyponitric acid, or nitric acid, either singly or mixed with one another, at the ordinary atmospheric temperature, or at an elevated temperature, until the production of the alizarine-orange is complete, or nearly so.

In every instance due care is to be taken to avoid the employment of any excess of the nitrogen acids, as such an excess would carry

the action too far, and have the ultimate effect of destroying the desired product.

As an example, I proceed as follows: I take a cold and saturated solution of alizarine in sulphuric ether, and I allow a current of nitrous acid to pass through it for some time, until a crystallization takes place, consisting of small shining scales of the alizarine-orange in an almost chemically-pure condition.

By another method I dissolve one part, by weight, of alizarine in about twenty parts, by weight, of nitro-benzole at a temperature of about 120° centigrade, and this solution, while being kept heated, I treat with a current of nitrous acid until no more absorption of the gas takes place, and the mixture no longer contains any appreciable quantity of unaltered alizarine. The alizarine-orange may then be separated from the nitro-benzole by removing the latter by distillation; or the mixture may be agitated with an aqueous solution of caustic or carbonated alkali until the coloring matter has been withdrawn from its solution in nitro-benzole. The alkaline compound of the alizarine-orange is afterward decomposed by a suitable acid—then filtered and washed.

Another method for effecting the conversion of alizarine into alizarine-orange by means of nitrous or hyponitric acids, and in presence of a suitable solvent, is the following: I take about one part, by weight, of alizarine in a finely-divided condition, which is intimately mixed with about thirty parts, by weight, of benzole, and the mixture is then heated to ebullition in a suitable vessel or apparatus, (by preference in an earthenware distillatory apparatus provided with a condensing arrangement,) in such a manner as that the benzole is constantly made to run back into the vessel. I then pass the gaseous mixture of nitrous and hyponitric acids into and through the boiling mixture of alizarine and benzole until the conversion of the former into alizarine-orange is complete, or nearly so. I then allow the mixture to cool, and separate the alizarine-orange from the benzole by filtration. The benzole which has served for this operation can afterward be conveniently used for a series of similar operations, or it may be recovered by distillation.

The following process I give as an example to illustrate the conversion of alizarine into alizarine-orange by means of nitric acid acting in presence of a suitable solvent of alizarine: About two parts, by weight, of alizarine are mixed with about twenty (20) parts, by weight, of glacial acetic acid, and with about one and a half ($1\frac{1}{2}$) part, by weight, of nitric acid of about 1.38 specific gravity, which are added by small portions at a time. The mixture is then allowed to remain tranquil for about twenty-four hours at the ordinary temperature; or I accelerate the action by employing a somewhat higher temperature—say, from about 30° to 50° centigrade. In this pro-

cess the glacial acetic acid may be replaced by other suitable solvents of alizarine—such as petroleum hydrocarbons, benzole, or its homologues, nitro-benzole, bisulphide of carbon.

The result of this operation is then freed from the solvents employed by filtration or otherwise, and ultimately washed and dried.

The alizarine-orange obtained by the above-described methods may, if desired, be converted into a paste by dissolving it in diluted caustic or carbonated alkalies, and precipitating the solutions thus obtained by a suitable acid. The precipitate is collected on filters, and, after being well washed, it is a coloring matter suitable for dyeing and printing.

A further purification of the alizarine-orange may be effected in various ways—as, for instance, by adding an excess of caustic potash or soda solution to its alkaline solution, and by redissolving the precipitate thus produced in water, and decomposing the solution by a suitable acid, when the purified coloring matter will be again precipitated, and may be filtered and washed, as above stated.

Another process for producing coloring matter, similar to the above-mentioned alizarine-orange, according to my invention, consists in dissolving pure or commercial alizarine in concentrated sulphuric acid, and treating the solution at the ordinary atmospheric temperature with nitrous hyponitric or nitric acids, or with a corresponding quantity of any saline compound of the same, the action of these acids or compounds being allowed to continue, with due care to avoid rise of temperature, until the solution no longer contains any or but little unaltered alizarine. As an example, I proceed as follows: I take about ten parts, by weight, of alizarine, which are dissolved in about fifty parts, by weight, of sulphuric acid of about 1.848 specific gravity, and this mixture is afterward cooled down to a temperature of about zero, and, by preference, not higher than 10° centigrade. I then add, in small portions, from time to time, and with due care, so as to avoid any rise of temperature, a well-cooled mixture of eight parts, by weight, of nitric acid of about 1.38 specific gravity, with about forty parts, by weight, of sulphuric acid of about 1.848 specific gravity. The mixture is then mixed with a large quantity of cold water, and the precipitate obtained filtered and well washed.

A further purification of the coloring matter may be arrived at by the methods before described.

According to a further portion of my invention, a coloring matter possessing the properties of purpurine may be obtained as follows: Upon dissolving one part, by weight, of the coloring matter obtained by the last-named process in about ten parts, by weight, of concentrated sulphuric acid of about 1.848 specific gravity, and by gradually raising the temperature of the solution to about 150° centigrade, an evolution of gas ensues, chiefly consisting of nitrogen, upon the cessation of

which the solution will be found to contain the coloring matter possessing the properties of purpurine, which coloring matter may be attained in a state suitable for dyeing and printing, by mixing the acid solution with water, and filtering and washing the precipitate thus obtained, which may or may not be further purified by the well-known methods for preparing pure purpurine—as, for example, by dissolving the coloring matter in a boiling and concentrated aqueous solution of alum, and by precipitating the coloring matter from the filtered solution by means of a mineral acid.

A similar result may be obtained by treating the sulphuric-acid solution of pure or commercial alizarine with nitrous hyponitric or nitric acids in the manner above described, until the production of alizarine-orange is complete, or nearly so, and afterward raising the temperature of the solution until the evolution of gas has ceased and the formation of purpurine is perfect, or nearly so. I then apply the methods above described for obtaining purpurine in a state suitable for dyeing and printing.

I wish it to be understood that I do not confine myself to the proportions, weights, periods, or temperature hereinbefore stated, as such may be varied; but the processes described will be found practically to serve as examples for carrying out my invention.

I claim—

1. Converting pure or commercial alizarine into alizarine-orange by the action of nitrogen acids, substantially in the manner herein set forth.

2. The production of alizarine-orange by the action of either nitrous or of hyponitric acids or mixtures of the same upon either pure or upon commercial alizarine, the same being obtained either from natural sources or produced artificially, and such alizarine or alizarines being employed either in their dried

condition or mixed with, or dissolved in, a suitable solvent not easily acted upon by the nitrogen and other acids employed.

3. The production of alizarine-orange by means of nitric acid acting in presence of a suitable solvent upon pure or upon commercial alizarine in the manner hereinbefore described.

4. In the production of an alizarine-orange from either pure or from commercial alizarine by first dissolving the same in concentrated sulphuric acid, and then heating the solution with either nitrous hyponitric or nitric acids, or with mixtures of the same, in the manner hereinbefore described.

5. In the production of a coloring matter possessing the properties of purpurine by dissolving alizarine-orange obtained by the process described in the foregoing claims of this specification in concentrated sulphuric acid, and then gradually raising the temperature of such solution in the manner hereinbefore described.

6. In the production of a coloring matter possessing the properties of purpurine by heating either pure or commercial alizarine dissolved in concentrated sulphuric acid, and then submitting such solution to the action of either nitrous hyponitric or nitric acids or mixtures of the same, so as to produce alizarine-orange, and subsequently raising the temperature of such solution, so as to produce the desired coloring matter, in the manner hereinbefore described.

In witness whereof I have signed my name to this specification in the presence of two subscribing witnesses.

HEINRICH CARO.

Witnesses:

W. GORTON,
Clerk to Mr. J. Henry Johnson, 47 Lincoln's
Inn Fields, London.

CHAS. MILLS,
47 Lincoln's Inn Fields, London.