

UNITED STATES PATENT OFFICE.

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CHEMICAL COMPANY, OF SAME PLACE.

BROWN PETROLEUM NITRO DYE.

SPECIFICATION forming part of Letters Patent No. 518,991, dated May 1, 1894.

Application filed April 19, 1893. Serial No. 471,018. (Specimens.)

To all whom it may concern:

Be it known that I, HANS A. FRASCH, a citizen of the United States, residing at Cleveland, in the county of Cuyahoga and State of Ohio, have invented certain new and useful Improvements in Methods of Obtaining Dye-
5 Stuffs from Hydrocarbons by Nitration; and I do hereby declare that the following is a full, clear, and exact description of the invention,
10 which will enable others skilled in the art to which it appertains to make and use the same.

In the manufacture of anilin, artificial alizarin, and kindred dyestuffs and bases for dyestuffs and colors, coal tar obtained from illuminating gas works has hitherto been employed. The ordinary process of conversion is by fractional distillation of the coal tar. The aromatic series of hydrocarbons contained in such coal tar furnishes the source
15 whence these dyestuffs or colors have been derived. A kindred or similar series of hydrocarbons exists also in petroleum or natural mineral oil or the distillates or derivatives, residual or otherwise, thereof; and it is
20 upon these hydrocarbons of the petroleum series as distinguished from the hydrocarbons of the coal tar series that I act for obtaining my new dyestuffs.

My invention relates, first, to a method of
30 obtaining dyestuffs from hydrocarbons contained in such natural oils by nitration, and second, to the product so obtained.

In practicing my invention, I subject crude petroleum or its distillates or products, residual or otherwise, to the action of a mixture
35 of sulfuric and nitric acids until all the aromatic hydrocarbons, olefines, naphthenes and unsaturated hydrocarbons in the oil are taken up in the acid mixture as oxidized and corresponding nitro products. I prefer to use one
40 part of nitric acid to three parts of sulfuric acid in the mixture, but these proportions may be varied; and so also the proportion of acid mixture to oil may be varied, according
45 to the quality of the oil being treated, and according to the quantity of sulfuric and other acids that may be in the petroleum or its products being treated. Crude oil requires about twenty-five per cent., while distillates
50 require from two to ten per cent., and sludge

from nothing to five per cent., according to the quantity of acid remaining in the substance. In all cases, the treatment proceeds alike, substantially as follows: The mixture of acid and oil is agitated, mechanically or
55 by a forced current of air, at ordinary temperatures say, 15° to 20° Celsius, until a sample from which the acid has been permitted to settle will discolor little, if any, upon the addition thereto of fresh concentrated acid.
60 The mixture of acid and oil is then permitted to rest until the acid is separated from the oil, when the acid containing the aromatic hydrocarbons and tarry substances is drawn from the oil. The acid mixture taken from
65 the oil is then heated to from 60° to 80° Celsius, until the hydrocarbons contained therein are converted into nitro or oxidized products. Nitration may be effected without heat
70 by keeping the mixture agitated a long time, say, from four to eight weeks, and even longer, thus permitting the acid to act upon the hydrocarbons. The requisite degree or extent
75 of nitration is determined when the bulk of a test sample will dissolve in a hot solution of alkali. The free acid is then removed and this may be readily accomplished by neutralization or repeatedly washing the mixture with
80 cold water or by precipitating the nitro compound from the acid. After the free acid is removed, the residuum is heated with water until the water is saturated with the more
85 soluble nitro products. The solution is left to settle, when the soluble products and the insoluble matter and oily matter are separated by decantation. The soluble products
90 are then drawn off and consist in a mixture of different higher or lower nitro products. To separate these products carbonate of lime or caustic soda is added, with or without
95 heating, until precipitation ceases, whereby a soluble and an insoluble calcium salt are obtained. Any other substance such as barium or lead, which will form a soluble and an insoluble salt with the nitro product may
100 be substituted for the calcium. The solution is separated from the precipitate, and a reddish brown dyestuff precipitated from the solution by addition, until precipitation ceases, of hydrochloric acid, sodium chlorid,

or any other salt in whose watery solution the dyestuff is insoluble. The dyestuff is then separated by filtration.

Instead of obtaining the dyestuff directly, as just described, it may be obtained indirectly by converting the calcium salt into a salt of potassium, ammonium, &c., and then separating the dyestuff as before.

The insoluble salt separated from the solution first above mentioned may be converted into a soluble salt by the addition thereto of carbonate of sodium, potassium, ammonium, or any other substance that will unite therewith and form a soluble compound or dyestuff and displace the calcium. The dyestuff itself is precipitated from the solution thereby obtained by the addition of hydrochloric acid, sodium chlorid, or any other salt in whose solution the dyestuff is insoluble.

The treatment of this insoluble salt and the dyestuff obtained therefrom form the subject-matter of an application filed by me as a division hereof, Serial No. 489,042, filed October 24, 1893.

The dyestuff obtained by the method first above described is in the form of a reddish brown powder, soluble in water and glycerin and acetone. In its solutions, and more especially its acetone solutions, it has a bluish green fluorescence. It forms a soluble calcium salt and emits the characteristic odor of burning coal oil when exposed to high heat. It dyes silk and wool, in acidulated solutions, without mordant, a reddish brown.

The dyestuff obtained by the second mentioned process is a distinct brown color and in the form of a powder. It has a resinous appearance or texture when first made, but can be pulverized. This dyestuff is soluble slightly in cold water, but readily soluble in hot water. It is also soluble in acetone and glycerin. It forms an insoluble calcium salt, and is thus mainly distinguished from the first named salt. It emits the characteristic odor of burning coal oil when highly heated, and dyes cotton, without mordant, a brownish color.

If instead of using a mixture of sulfuric acid and nitric acid, sulfuric acid be substituted in the process above described, a sulfo product will be obtained. In contemporaneous applications (Serial Nos. 471,016 and 471,017, filed April 19, 1893) I have fully described this sulfo process and product, and to them reference is hereby made for further particulars. The sulfo product referred to may be treated to obtain a nitro product by dissolving the finished sulfo product in water and heating it with nitric acid until effervescence ceases, after which the product is precipitated from the solution as before. The same or a similar body may be obtained by the addition to a watery solution of the sulfo product of sodium nitrite and hydrochloric acid, and it can be obtained also by the addition of nitrous acid to the sulfo product.

What I claim is—

1. The art of manufacturing dyestuffs by nitration of petroleum, natural mineral oils, or the residuum of the distillation or refining thereof, with nitro-sulfuric acid, washing the resulting products with water, then heating with water, allowing the insoluble matter to settle, and removing the solution from the sediment and treating it with a base, such as lime, and thereby forming a soluble and an insoluble salt, and precipitating from the soluble salt solution the dyestuff by the addition of a reagent, such as sodium chlorid, substantially as described.

2. As an article of manufacture, a petroleum product which is a nitro body in the form of a reddish brown powder, soluble in water, glycerin, and acetone, and which is capable of dyeing wool or silk, without mordant, a reddish brown color, and whose calcium salt is soluble in water, substantially as described.

Witness my hand to the foregoing specification.

HANS A. FRASCH.

Witnesses:

H. T. FISHER,
GEORGIA SCHAEFFER.