

UNITED STATES PATENT OFFICE.

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CHEMICAL COMPANY, OF SAME PLACE.

PETROLEUM DYE.

SPECIFICATION forming part of Letters Patent No. 518,992, dated May 1, 1894.

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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 the Art of Producing Dye-Stuffs from Natural Mineral Oils by Sulfonation; and I 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 utilization of such hydro-carbons as natural mineral oil or petroleum or the distillates or derivatives thereof for obtaining dyestuffs or color bases.

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 whence these dyestuffs or colors have been derived. A kindred or similar series of hydrocarbons exists also in petroleum or natural mineral ores or the distillates or derivatives, residual or otherwise, thereof, and it is upon this hydrocarbon of the petroleum series as distinguished from the hydrocarbons of the coal tar series that I act for obtaining my new dyestuff or color base.

My invention consists in the art or method of treating natural mineral oils, petroleum, or their derivatives or distillates by transforming or converting the same into coloring matter or dyestuff by subjecting them to the action of suitable reagents.

My invention also consists in the method of obtaining dyestuffs or color bases.

My invention also consists of a dyestuff or color base extracted from such substances and possessing and having as a distinguishing characteristic the property of emitting the odor of coal oil when highly heated.

My invention also consists in certain details as hereinafter more particularly set forth and claimed.

In practicing my invention, I subject crude petroleum or its distillates or products, re-

sidual or otherwise, to the action of sulfuric acid until all the aromatic hydrocarbons, olefines, naphthenes and unsaturated hydrocarbons in the oil are taken up in the acid as oxidized and corresponding sulfo products. The proportion of acid to oil varies greatly according to the quality of the oil being treated. Crude oil requires about twenty-five per cent. while distillates 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 by a forced current of air, until a sample from which the acid has been permitted to settle will discolor little if any upon the addition thereto of fresh concentrated sulfuric acid. 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 is then heated until the hydrocarbons contained therein are converted into sulfo combinations and oxidized products.

Sulfonation may be effected without heat by keeping the mixture agitated for a long time, say, from four to eight weeks, and even longer, thus permitting the acid to act upon the hydrocarbons. Fuming or so-called Nordhausen sulfuric acid, or a mixture of chromic and sulfuric acids may also be employed for sulfonation. The requisite degree or extent of sulfonation is determined when the bulk of a test sample will dissolve in a hot solution of alkali. The free sulfuric acid is then removed, and this may be readily accomplished by neutralization or repeatedly washing the mixture with cold water or by precipitating the sulfo compound from the acid. After the free acid is removed, the residuum is heated with water until the water is saturated with the more soluble products. The solution is left to settle, whereby the soluble products and the insoluble and oily matter are separated. The soluble products are then drawn off and consist of a mixture of different higher or lower sulfo products. To separate these products calcium carbonate or

hydrate is added with or without heating until precipitation ceases, whereby a soluble and an insoluble calcium salt are obtained. Any other substance which will form a soluble and an insoluble salt with the sulfo product may be substituted for the calcium. The soluble and insoluble salts are then separated by filtration or other means. The dyestuff is precipitated from a solution of this soluble salt by the addition thereto of chloride of sodium or any other salt in which the dyestuff is insoluble. The dyestuff may be obtained also by transforming the soluble salt above mentioned into a salt of sodium, potassium, ammonium, &c., by the addition thereto of sodium carbonate, potassium carbonate, ammonium carbonate, &c., or any other base which has the capacity of displacing the base already represented in the solution. From the solution thus last obtained the dyestuff may be precipitated as before, as, for example, by the addition of sodium chlorid.

The dyestuff is obtained in the form of a yellow powder, soluble in water, alcohol and glycerine and also soluble in most of the aromatic hydrocarbons. Its solutions have a greenish fluorescence. The dyestuff emits the characteristic odor of coal oil when highly heated. It dyes wool and silk in acidulated solution a bright yellow. If exposed to the action of nitrous or nitric acid it produces a dyestuff of a reddish brown color.

What I claim is—

1. The method of producing dyestuff from petroleum by subjecting natural mineral oil, the distillates or residuums of the distillation

or refining thereof, to sulfonation, washing the products of sulfonation with water, treating the products soluble in hot water with a base, such as lime, and isolating from the sulfo salts thereby obtained a dyestuff by treatment with an alkali and then with a precipitant, such as sodium chloride, substantially as described.

2. The method of producing a yellow dyestuff from petroleum, which consists in subjecting natural mineral oil, the distillates or residuums of the distillation or refining thereof, to sulfonation, leaching the products of sulfonation with water, treating the products soluble in hot water with a base, such as lime, and saturating the solution thereby obtained with a suitable reagent, such as sodium chloride, and thereby precipitating a yellow dyestuff, substantially as described.

3. As an article of manufacture, sulfonated petroleum hydrocarbon, which is capable of dyeing wool or silk, in acidulated solution, without mordant, substantially as described.

4. As an article of manufacture, a sulfo body of the petroleum series of hydrocarbons, solid in form, having a yellow color, soluble in water, glycerine, and acetone, fluorescent in solution, and dyeing wool or silk, without mordant, in acidulated solution, a canary yellow color, substantially as described.

Witness my hand to the foregoing specification.

HANS A. FRASCH.

Witnesses:

H. T. FISHER,
GEORGIA SCHAEFFER.