No. 622,799. Patented Apr. 11, 1899.

H. FRASCH.

PROCESS OF AND APPARATUS FOR PURIFYING PETROLEUM.

(Application filed Nov. 7, 1888.)

(No Model.) 2 Sheets—Sheet 1.

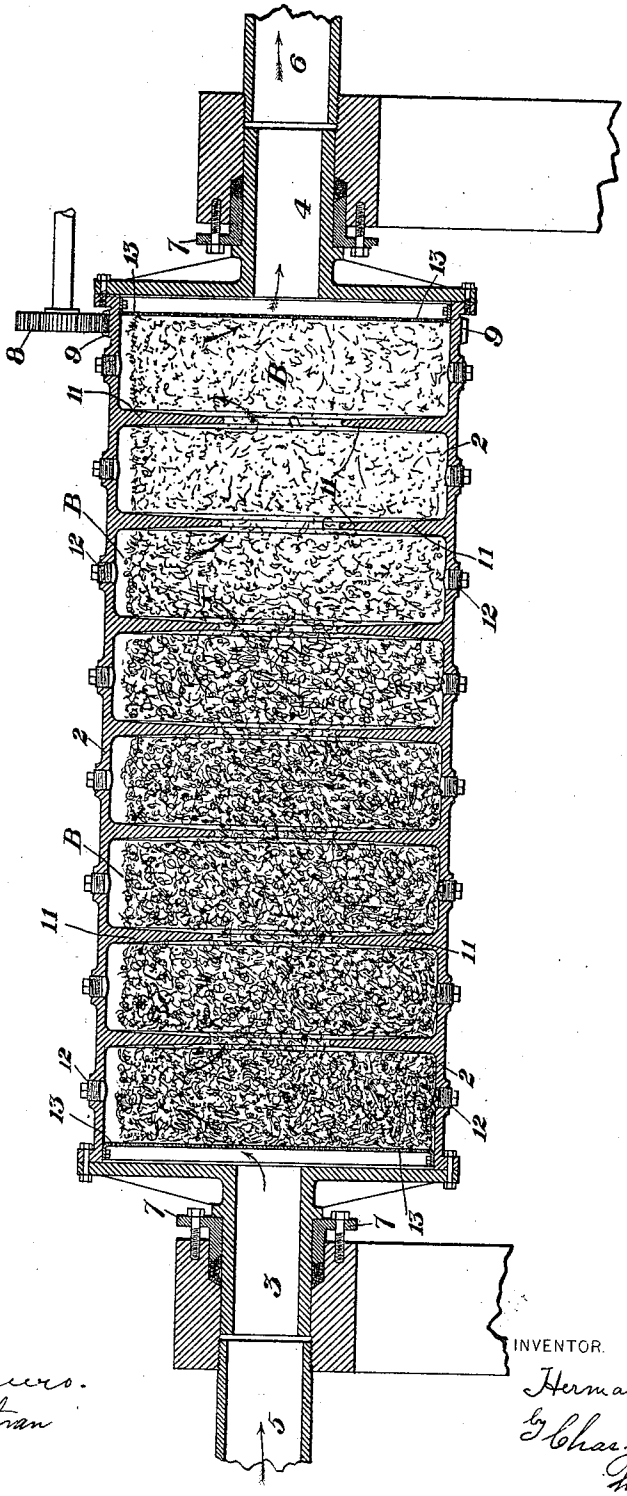


Fig. 1

WITNESSES.

Philip Mauro.

Jas. K. McCutchan

INVENTOR.

Herman Frasch

by Chas. J. Hedrick

his attorney

THE NORRIS PETERS CO., PHOTO-LITHO., WASHINGTON, D. C.

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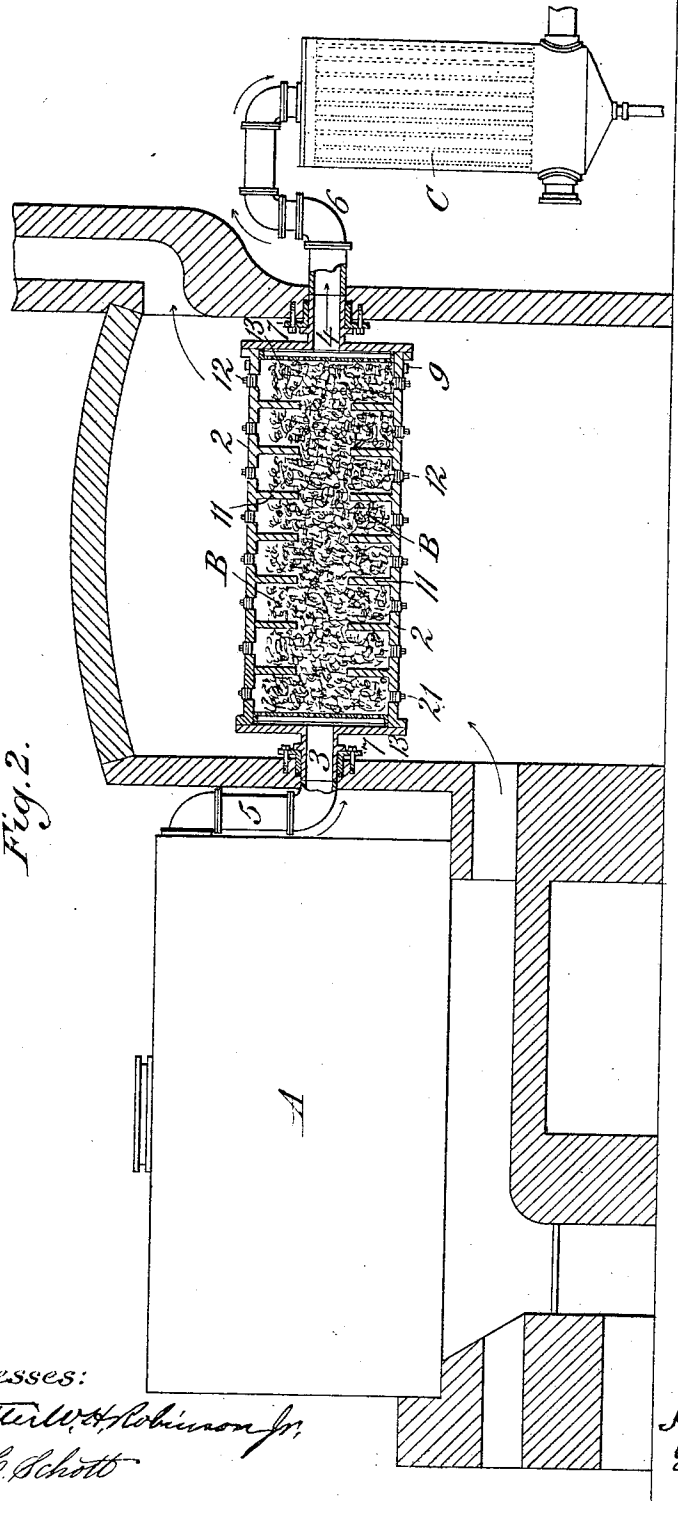


Fig. 2.

Witnesses:
Walter W. Robinson Jr.
F. H. Schott

Inventor:
Herman Frasch
by Chas. J. Hedrick
his attorney

THE NORRIS PETERS CO., PHOTO-LITHO., WASHINGTON, D. C.

UNITED STATES PATENT OFFICE.

HERMAN FRASCH, OF CLEVELAND, OHIO, ASSIGNOR TO THE SOLAR REFINING COMPANY, OF OHIO.

PROCESS OF AND APPARATUS FOR PURIFYING PETROLEUM.

SPECIFICATION forming part of Letters Patent No. 622,799, dated April 11, 1899.

Application filed November 7, 1888. Serial No. 290,198. (No model.)

To all whom it may concern:

Be it known that I, HERMAN FRASCH, of Cleveland, in the county of Cuyahoga and State of Ohio, have invented new and useful Improvements in Processes of and Apparatus for Purifying Petroleum; and I do hereby declare the following to be a full, clear, and exact description thereof.

This invention relates to an improvement in the art of purifying a certain class of petroleum generally known as "Canadian oil" or "Lima oil," so called because chiefly found in Canada and at Lima, in the State of Ohio, and characterized by the presence of considerable proportions of sulfur compounds, which resist the ordinary treatment for the removal of sulfur and give to the oil a peculiarly disagreeable and penetrating odor, rendering it unfit for general use. The sulfur compounds in such oils may be removed and the oils deodorized by subjecting the oil either while in a liquid state or in form of vapor to contact with a metal or metals in finely-divided particles. The sulfur compounds of the oil then unite with the metal purificator, forming a sulfid of the metal; but in practice it is found that the surface of the metal so soon becomes coated with the sulfid as to render it inactive, or practically so, for purpose of purification, and unless some suitable means be employed for cleansing the metal, so as to present fresh metallic surfaces to the sulfur compounds of the oil, this process of purification cannot be practiced without the use of such enormous quantities of the purifying material as to render the expense out of proportion to the end to be attained thereby. Nearly all metals may be used in this process of purification, and I have found that copper, lead, mercury, and the others of that class of metals which may be precipitated from acid solutions by hydrogen sulfid, as well as the metals of the alkaline and earthy series, will abstract the sulfur compounds from the petroleums at all temperatures, though their affinity therefor is generally increased by elevation of the temperature. Those metals—such as iron, zinc, tin, antimony, &c.—which are precipitated as sulfids from their solutions by sulfid of ammonia, but whose sulfids are decomposed by hydrochloric acid, are somewhat less energetic. I have found that copper is especially adapted for use in this process, it being employed in a finely-divided state either alone or alloyed with some cheaper metal or deposited thereon either galvanically or chemically by exchange of solvent, as in case of the addition of sulfate of copper to metallic iron or otherwise or being deposited in or on other suitable carrier—as, for example, plaster, ground-up iron ore, and the like.

In the practical use of a metallic purificator it may be added in a very finely divided form to the oil in the still during the process of distillation and kept in suspension in the oil by suitable agitators, or the oil-vapors may be purified by passing them through a vessel or filter containing the metal in the form of small particles, which filter is preferably heated in order to prevent condensation of the vapors and to facilitate the chemical action of the metal on the sulfur compounds. The oil in the liquid state may also be treated with the purifying metal without distillation.

My present invention consists in a process of cleansing the surface of the metal purificator by removing therefrom the sulfid coating which has formed thereon, and thus rendering the remaining metal capable of repeated and efficient use.

I shall describe my invention with especial reference to its use in the purification of petroleum-vapors after they have been given off from the oil in distillation, and from such description its use in connection with the analogous process of purification by introducing the purifying material into the oil in distillation in the still or in connection with other processes wherein such sulfid coating is formed will be readily understood.

Briefly stated the process which I employ consists in subjecting the sulfid-coated metals, either subsequently to or during the process of purification of the oil, to frictional agitation of its particles among each other, with or without foreign particles, so as to abrade and remove the coating of sulfid and to expose fresh metallic surfaces. This treatment is applicable to the treatment of metals used in the purification by agitating the purifying material in the still only after the completion of the purification, when the met-

als have settled to the bottom; but in purifying petroleum-vapors after they have been given off the agitation and abrasion may be performed either after the use of the metals has been completed or simultaneously therewith.

The invention also consists in the treatment of the coated metals with a solvent of the metals or of the metallic sulfids. In using a solvent of the metallic sulfid this may decompose the sulfid coating, liberating hydrogen sulfid gas and forming a soluble salt as a sulfate, for example, of the metal, in case sulfuric acid be employed as the solvent, which sulfate may be removed by washing with water. This step (cleansing with a chemical solvent) may be used in combination with the mechanical abrasion of the metal or may be omitted altogether.

Many different forms of apparatus may be employed in the practice of my invention, and I do not desire to limit its scope to any particular means therefor. I have, however, devised a form of apparatus especially well adapted for the practice of my invention where the petroleum is desulfurized when in a vaporous condition. This apparatus also forms part of my invention, and consists in the combination, with a petroleum or oil still and a condenser for the oil-vapors, of an interposed agitatory or rotary vessel for containing and cleansing a purificator and means for heating said vessel.

My invention also includes the other improvements or combinations hereinafter set forth.

The purifier vessel is shown in longitudinal section in the accompanying drawings, which form part of this specification, and in which—

Figure 1 shows the said purifier vessel by itself, and Fig. 2 in connection with a still and a condenser.

In the drawings, 2 is a rotary column or drum having at the opposite ends a hollow shaft 3, forming a vapor-inlet pipe, and a hollow shaft 4, forming a vapor-outlet pipe, which also serve as the journals of the rotary drum and have their bearings at one end in the vapor-pipe 5, which leads from the oil-still A, Fig. 2, and at the other end in the vapor-pipe 6, which leads to the condenser C, Fig. 2. The drum is shown as inclosed in the chamber D, through which the products of combustion from the fire-chamber E under the still A are conducted on their way to the chimney F. Suitable packing is placed in stuffing-boxes at the joints of the shafts 3 and 4 with the pipes 5 and 6 and is confined by followers or glands 7, of the usual construction.

The drum 2 is adapted to be rotated either by a belt connection from a suitable motor or, as I have shown in the drawings, by a pinion 8, which engages with an annular series of cogs 9, disposed around the periphery of the drum. The interior of the drum is divided into a series of compartments B by annular cross-partitions 11, the central openings of which are preferably about one-half of the internal diameter of the drum, and each compartment is provided with diametrically opposite charging and discharging holes—say of about two inches in diameter—each of which is fitted with a removable plug 12. The two end compartments of the drum are closed by perforated or grated partitions 13, which permit the free passage of vapors from and into the hollow shafts or trunnions 3 4, but prevent the entrance of the solid purifying material thereinto. Each of the compartments B is charged with the metallic purifying agent in the form of divided particles or pieces, so that a large surface area of the purificator shall be presented to the passing vapors. If iron is used as the purificator, either alone or coated with copper, iron borings from a machinist's lathe are admirably adapted to the purpose. The metal in each compartment should be sufficient in quantity to fill it above the level of the central openings in the annular partitions, since otherwise there would be an unobstructed course for the passage of the vapors over the purifying metal, instead of through it, and the purification would therefore be defective and insufficient. During the process of distillation the vapors from the still pass through the drum, and the latter is either rotated continuously or intermittently. In its passage through each of the series of compartments B the vapor must ascend through the metal toward the top of the compartment and then descend, as shown by the arrows in the drawings, and pass through the central hole in the partition into the next compartment, and so on, so that it is brought into intimate contact with the metal and is thoroughly desulfurized. The advantage of using these partitions is that otherwise the contents of the drum, although originally filling it as completely as possible, would eventually settle, leaving an unobstructed passage for the vapors, and by making the openings in the partition small relatively to the diameter of the drum a very considerable diminution or settling of the purifying material may occur without materially affecting the efficiency of the apparatus.

As I have before stated, the contact of the vapors with the surface of the metal purifying agent causes the formation of sulfids on the surface of the latter; but by the tumbling caused by the rotation of the drum and the consequent abrasion of the metal particles the sulfid is removed, and fresh metallic surfaces are laid bare. At the end of each run from the still the abraded particles of sulfid may be washed out by water poured into the charging-holes and drawn off from the holes on the opposite side of the drum. I prefer to carry on this agitation and consequent abrasion continuously during the passage of the vapors through the drum, because the material is then constantly being renewed by the exposure of fresh uncoated metallic surfaces, and I am enabled to purify the oil with

the use of a much smaller quantity of the metal than would otherwise be necessary. The agitation may, however, be performed only at intervals or at the end of each run from the still, and, if desired, instead of using the same column or drum both for the passage of the vapors and for the agitation and abrasion of the metal the metal may be removed from the purifier at the end of each run and tumbled or agitated in another vessel. The latter mode is that which I practice in the cleansing of the metallic purificator after it has been used in purifying liquid petroleum or petroleum distillate. The metal after it has settled to the bottom of the still is removed, dried, and, if necessary, roasted, reduced, and then agitated in a drum of the character shown in the drawings or in some other suitable tumbling apparatus.

Although the tumbling and abrasion of the metal in the drum 2 is sufficient to remove much of the sulfid coating, it may not be sufficient to entirely cleanse it, and I therefore prefer from time to time—say after each run—to further cleanse the metal by a chemically-acting liquid. I have found that such cleansing can be effected by pouring through the sulfid-coated metal a liquid solvent of the metal or of the metallic sulfid. In the case of iron, for example, the sulfid will be decomposed, forming a sulfate, if sulfuric acid was employed, with the liberation of hydrogen-sulfid gas. I have found dilute sulfuric acid (one part of H_2SO_4 and six parts of water) with the addition of a small quantity—say one-half of one per cent.—of nitric acid, if found necessary, well adapted to this end in the cases in which it is a solvent of the metal used or its sulfid, though other acids—such as hydrochloric, nitric, or acetic—may be employed. Should stronger acid than the dilution named be required to attack the coating-sulfid or the underlying metal, it may be used. I pour this cleansing liquid into the vessel containing the coated metal, allowing it to percolate through the mass, adding fresh quantities from time to time at intervals, say, of ten or fifteen minutes, until the diminution of evolution of hydrogen sulfid gas or the absence of the metallic sulfid in the outflowing liquid indicates the approximate cleansing of the metal. In thus cleansing the metal while in the drum 2 the cleansing liquid is poured into the compartments through the charging-holes at one side of the drum and drained off at the holes at the opposite side, and when the acid washing is completed the metal is further cleansed from the acid by pouring water through the compartments. If desired, the cleansing of the material by chemical solvents may be omitted.

In the use of the apparatus shown in the drawings for the purification of petroleum-vapors I suggest the use with a hundred-barrel still of a column of about twelve feet in length and forty-eight inches in diameter. This column may be heated, preferably, to about the temperature of the oil-vapors either by a suitable furnace or by being placed in the waste-flue of the furnace of the still, and to secure uniformity of purification of the petroleum product uniformity of temperature should be maintained. I desire, however, to indicate clearly that my invention, broadly considered, is not limited to the use of any special form of apparatus, neither to the use of a combined agitating and purifying apparatus nor to the use of a rotary agitator, since the agitation may be performed by shaking or the longitudinal or lateral reciprocations of the agitator as well as by the rotation thereof.

The apparatus is susceptible of other modifications also by those skilled in the art. For example, the cross-partitions of the drawings may be omitted or may be otherwise constructed. In some cases it may be desirable to use the drum as a stationary vessel having upright partitions. I intend, moreover, to claim specifically, in addition to the broad claims of this patent, that form of apparatus which I show and describe herein, since it possesses certain intrinsic advantages. Those of the hereinafter-written claims which are numbered from 6 to 9, both inclusive, have been transferred from the specification of my application, Serial No. 297,694, filed January 26, 1889 to this specification, (which always described the apparatus on which said claims are based,) all my rights under both of my said applications—namely, Serial Nos. 290,198 and 297,694—being continued and preserved by the present patent. In still another application, Serial No. 289,280, filed October 27, 1888, I claim the use as a detergent of a chemical solvent of the sulfid coating or of the metal constituting said purificator.

The passage of the petroleum-vapors through a mass of solid purifying material in a proper state of division, kept in agitation more or less continuously during such passage, is useful with purifying materials in general—say, for example, those specified in my patent of February 21, 1888, No. 378,246—since it prevents the vapors from making paths of least resistance for themselves and brings about the reaction with all parts of said mass; but it is specially useful with metallic particles on account of the further effect of exposing the metallic surfaces.

Under the term "solid purificator" as hereinafter employed I include solid purifying material in general in a suitable state of division, as well as metal borings or similar metallic particles.

I claim as my invention—

1. As an improvement in the art of purifying petroleums of the Canadian or Lima class, for the removal of the offensive sulfur compound contained therein, passing the vapors of distillation through a column or vessel containing metallic purifying material in divided particles, such vessel being revolved or agitated constantly or intermittently dur-

ing the passage of the vapor therethrough for the purpose of removing from their surfaces, by the abrasion on each other of the particles of the purificator, the metallic sulfid which is formed thereon, substantially as described.

2. As an improvement in the art of purifying petroleums of the Canadian and Lima class, which are distinguished by their offensive odor, subjecting such oil or its vapor of distillation in a suitable vessel to metallic matter, such as iron borings, in divided particles, which are subjected to frictional agitation by the rotation or agitation of the vessel while the oil or its vapor is present therein, for the purpose of bringing such oil or vapor into more intimate contact with the metallic matter and of removing from the surfaces of the metallic particles the sulfid of such metal formed thereon, so as to increase the efficiency of the metal particles by laying bare fresh surfaces, substantially as described.

3. As an improvement in the art of purifying petroleum of the Canadian and Lima class, by passing the vapors of distillation into a vessel charged with divided particles of a metallic purificator capable of combining with the offensive sulfur compound contained in such oil, producing frictional agitation of the particles of purificator for separating therefrom the surface-coating of metallic sulfid, resulting from the reaction produced thereby, by the agitation of the particles of purificator within the vessel, in combination with the introduction into said vessel of a solvent of the metal or metallic sulfid, to aid in the cleansing of the purificator, substantially as described.

4. The improvement in the art of purifying petroleum of the Canadian and Lima class by removal of the skunk therefrom, consisting in passing the vapors of distillation thereof through a vessel charged with divided solid metallic matter adapted to combine with the offensive sulfur compound together with suitable foreign matter adapted to aid in the separation of the surface-coating of sulfid by abrasion and frictional attrition of the solid contents of the vessel upon each other, effected by the rotation or agitation of said vessel, substantially as described.

5. As an improvement in the art of purifying petroleums of the Canadian and Lima class, for the removal of the offensive sulfur compound contained therein, by subjecting oil of this class or the vapor of such oil to the action of metallic particles so as to form a compound of the metal with the sulfur in the said compound, the denuding of the said particles of their coatings of sulfur metallic compound by agitation of the so-coated particles in contact with one another in a loose mass in a revolving or agitated column or vessel, the oil or its vapor being subjected to the so-denuded particles, substantially as described.

6. An improvement in means for purifying petroleum of its sulfur content, during distillation, consisting of the combination with a petroleum-still, and means for heating said still, of a rotary vessel containing a solid purificator such as described, interposed, in the path of the vapors of distillation, between the still and condenser, and means for heating said vessel, substantially as described.

7. The combination with a petroleum-still, and a condenser, of an agitatory or rotatory vessel for containing and cleansing a purificator interposed in the path of the vapors between the said still and condenser, and means for heating said vessel, substantially as described.

8. The combination with a petroleum-still, and a condenser, of an agitatory or rotatory vessel partly filled with a granular purificator so that the particles may grind upon one another and provided with means for forcing said vapors to pass below the level of said purificator, and means for heating the said vessel, the said vessel being interposed in the path of the vapors between the said still and the said condenser, substantially as described.

9. The combination with a petroleum-still, and a condenser, of an agitatory or rotatory vessel divided into compartments by cross-partitions provided with central openings and imperforate margins at the periphery interposed in the path of the vapors between the said still and the condenser, and means for heating said vessel, substantially as described.

In testimony whereof I have hereunto set my hand this 27th day of October, A. D. 1888.

HERMAN FRASCH.

Witnesses:
F. W. LOTHMAN,
W. H. SMITH.