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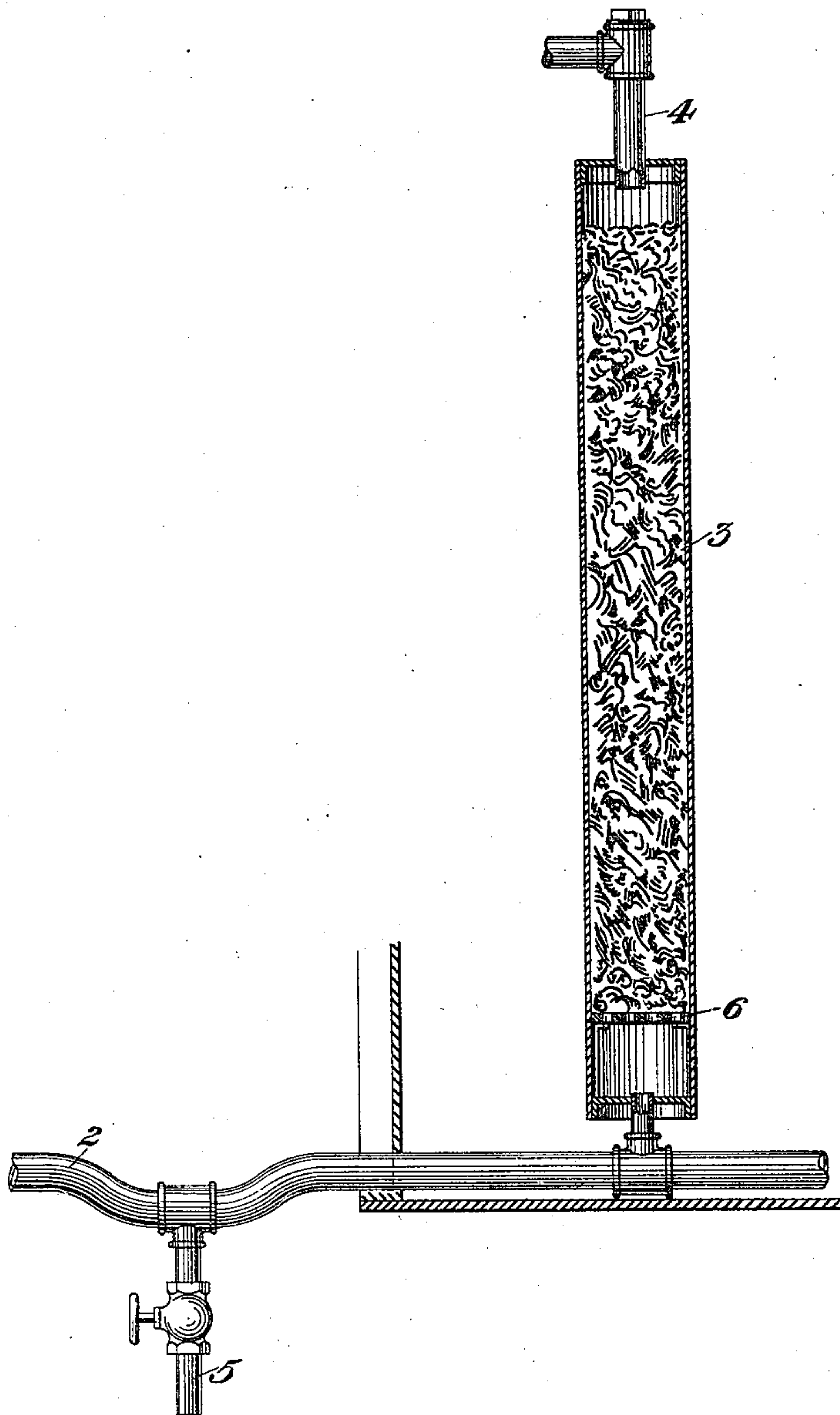
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H. FRASCH.

CLEANSING PURIFYING AGENT EMPLOYED IN PURIFYING PETROLEUM.

(Application filed Oct. 27, 1888.)

(No Model.)



WITNESSES

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UNITED STATES PATENT OFFICE.

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CLEANSING PURIFYING AGENT EMPLOYED IN PURIFYING PETROLEUM.

SPECIFICATION forming part of Letters Patent No. 630,496, dated August 8, 1899.

Application filed October 27, 1888. Serial No. 289,280. (No specimens.)

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 a new and useful
5 Improvement in Cleansing Purifying Agents Employed in the Purification of Petroleum; and I do hereby declare the following to be a full, clear, and exact description thereof.

My invention relates to an improvement
10 pertaining to the purification of oils containing sulfur compounds, especially that class of petroleums known as "Canadian" oil or "Lima" oil and distinguished by the presence of sulfur compounds which resist the ordinary
15 treatment for the removal of sulfur and which render the oils unfit for general use on account of their very disgusting odor. Such oils contain sulfur in large quantities, usually over one-half of one per cent., and derive
20 their ordinary names from the fact that they have been found chiefly in Canada and at Lima, in the State of Ohio. The peculiar malodorous sulfur compounds of these oils have received among the workers therein the
25 suggestive name of "skunk."

In the purification and deodorizing of Canadian and Lima oils it has been found that passing the vapors of such oil through a heated vessel or column charged with metallic iron,
30 copper, or other suitable metal in a divided state, such as borings, the metal deprives the oil-vapors of their sulfur compounds with the formation of metallic sulfids; but a serious difficulty in the practice of such process arises
35 from the fact that the coating of the metal with the sulfid soon destroys or at least diminishes its activity to such degree that the desulfurization of the oil-vapors becomes of so low an order as to be of no practical value.

40 The object of my invention is to revivify or renew the activity of the charge of purifying material when in consequence of the coating of the particles it has become spent or inactive, in order that the process of purification
45 may be carried on economically and without the very great labor and waste of material which must otherwise be spent in repeatedly recharging the purifying vessels or filters with fresh metal.

50 The invention is based on the discovery made by me that the coating of sulfid of iron

or other metal formed in decomposing the sulfur compounds of the oil-vapors can be removed by treating or washing the coated or inactive purifying metal with a liquid in
55 which the metal or the metallic sulfid is soluble with or without decomposition of said sulfid, so as to leave the iron or other metal as active (if not more so) in removing the sulfur compounds from the petroleum-vapors as it
60 was originally. Thus, for example, in the case of antimony, which I have found to be useful, as well as copper and iron, in removing the sulfur compounds, the sulfid may be dissolved in a solution of the alkaline sulfids with-
65 out decomposition, and in the case of copper the sulfid coating may be removed by a solvent, as dilute sulfuric acid having mixed therewith a small proportion of nitric acid, which solvent attacks the substance of the
70 purifying material underlying the sulfid and destroys the adhesion of the sulfid. The cleansing liquid or solution is drained off, and the portion which adheres to the metallic particles is preferably washed off with water. 75

Ordinarily it is preferred to employ iron in the purifier, both because of its cheapness and the ready solubility in dilute acids of the sulfid formed by its reaction with the sulfur compounds of the oil, the dilute acids, such
80 as dilute sulfuric acid, hydrochloric acid, nitric acid, or acetic acid, being (when solvents) the most economical and useful liquids for washing off the sulfid coating. Of course
85 if these or any one or more of them are not solvents of the sulfids of the metals employed in the purifier or of the metals or purifying materials which become coated use is to be made of liquids which are solvents thereof.

In practicing my invention I may either
90 wash the metal with acid while it is in the purifying vessel or filter or the metal may be removed from the filter and then washed and replaced; but I prefer to wash it while in the filter on account of the saving of labor of
95 handling the material, and I shall so describe the process.

The filter or purifying vessel containing the metallic purifying material may be of any convenient form suitable for the passage
100 through it of oil-vapor from the still. It is, however, conveniently made of an iron pipe

or column—say of eight inches diameter and six feet in length—having an opening at the top for charging it with metal in the form of borings or other small particles from which the pulverulent portions have been sifted, and at the base of the column is a tap for removing the washing liquid. The metal is supported in the column on a grating placed on legs, below which the vapor-pipe from the still enters, the purpose of which construction is to allow the vapors free passage into and through the iron particles. The distilling operation is carried on in the usual way and the vapors passed through this apparatus and purified by chemical combination of the sulfur compounds with the surface of the metal. When the metal has been coated with sulfid and its activity spent after each run from the still, as above described, I pour into the top of the column a quantity of dilute sulfuric acid (or other suitable acid) and allow it to percolate through the mass of iron particles in the column. In a column of the dimensions above described a suitable quantity of acid for this purpose is one quart of dilute sulfuric acid, (one part of H_2SO_4 and five parts of water,) to which may be added a small quantity—say one-half of one per cent.—of nitric acid introduced every few minutes though the quantity and strength may be somewhat varied. The addition of nitric acid to the dilute sulfuric acid should be made if copper constitutes the purifier. The so-prepared dilute acid attacks the metal under the sulfid coating and removes the latter mainly undissolved in the form of metallic sulfid, although some copper sulfate is produced. When iron is the purifier, the nitric acid addition is unnecessary, and in passing through the mass of metal in the filter the acid combines chemically with the coating of metallic sulfid, liberating hydrogen-sulfid gas and forming sulfate-of-iron solution. I add successive quantities of the dilute acid—say a quart at a time—at intervals of, say, five or ten minutes until the evolution of hydrogen-sulfid gas ceases, the cessation of which indicates that the sulfid of iron has been entirely dissolved. The chemical action of the acid may be hastened by heating the column and its contents to a temperature of, say, 212° Fahrenheit. As the acid percolates through the column it escapes from the outlet at the base, which is left open for this purpose, and at the end of the treatment with the dilute acid the metallic sulfate is cleaned out of the column by pouring water through it from the top, which descends through the mass of iron and escapes at said outlet. After it has been thus washed with water the column may be heated and its contents used for the purification of vapors by passing them through the column over or among the cleansed or renewed pieces or particles of iron therein.

As I have already indicated, my invention is not limited to the use of any precise form of apparatus for carrying it into effect; but

for the purpose of more clearly illustrating it I have prepared the accompanying drawing, forming part of this specification, which shows in vertical section the apparatus which I prefer to use.

In the drawing, 2 represents the vapor-outlet from the still.

3 is the column or vessel containing the metallic iron, communicating with the vapor-outlet and situate in the heat-flue of the furnace of the still.

4 is the pipe from which the vapors pass to the condenser after their passage through the column.

5 is the outlet at the base of the column, through which the acid and water are drawn after their percolation through the metallic contents, and 6 is the grate on which the metal is supported in the column.

With other metals whose sulfids are soluble in acids or other liquids with evolution of hydrogen sulfid the same procedure may be followed. When the sulfid is dissolved without decomposition in the wash or cleaning liquid employed, the said liquid as it is drawn off can be tested and the treatment ended when it no longer contains sulfid of the metal used in the purifier, or other modes of testing may be used. I of course do not limit myself to such details, which can be varied without departing from the spirit of the invention.

The invention is also applicable to revivifying or renewing metal which becomes coated with sulfid in purifying oil by bringing it in a liquid state in contact with the metal. It is applicable to the treatment of sulfur-containing oils in general whose sulfur is removable by metal, as well as to oil of the Canadian or Lima class. Moreover, the invention extends generally to cleansing solid purifying material in a suitable state of division whose particles have become coated in effecting the removal of sulfur from Lima or Canadian oil or other sulfur-containing oil by washing the coated material with a solvent.

I claim—

1. As a step in the process of removing the sulfur compounds, known as "skunk," from skunk-bearing petroleums, by the subjection of such oil or its vapors of distillation, in a heated vessel, to a metallic purifying agent or purifier, in a fragmentary condition, whereby the particles of such metallic purifier become surface-coated with its sulfid, the removal or separation of such sulfid coating from the purifier when so coated, by subjecting it to the action of a solvent, either of the sulfid or of the metallic substance coated therewith, whereby the sulfid coating is loosened and detached from its surface, either by being itself dissolved in the solvent or separated by the action of the solvent on the surface of the purifier; substantially as described.

2. As a step in the process of removing the sulfur compounds, known as "skunk," from skunk-bearing petroleums, by the subjection

of such oil or its vapors of distillation, in a heated vessel, to a metallic purifying agent or purificator, in a fragmentary condition, whereby the particles of such metallic purificator become surface-coated with its sulfid, the removal or separation of such sulfid coating from the purificator when so coated, by subjecting it to the action of dilute acid which is a solvent, either of the sulfid or of the metallic substance coated therewith, whereby the sulfid coating is loosened and detached from its surface, either by being itself dissolved in the solvent or separated by the action of the solvent on the surface of the purificator, substantially as described.

3. The process of removing the sulfur compounds, known as "skunk," from skunk-bearing petroleums, by employing together the two following steps, namely that step which consists in subjecting the skunk-bearing oil or its vapors of distillation, in a heated vessel, to a metallic purifying agent or purificator, in fragments from which the sulfid coating formed by a previous reaction of the metal with the skunk has been removed by a

chemical solvent of the metal or of its sulfid, and the step of removing or separating such sulfid coating from the said purificator by subjecting the so-coated purificator to the action of such solvent, substantially as described.

4. In the art of removing the sulfur compounds known as "skunk" from skunk-bearing petroleum by subjecting such petroleum or the vapors thereof to small pieces of metal, the improvement consisting in the combination with such subsection of the additional step of introducing dilute acid into the purifier vessel among the said pieces of metal, and thereby removing the films left by the reaction of the surface metal and the skunk and enabling the underlying metal to be utilized for subsequent reaction without removal of the metallic pieces from the said purifier vessel, substantially as described.

In testimony whereof I have hereunto set my hand this 11th day of October, A. D. 1888.

HERMAN FRASCH.

Witnesses:

W. B. CORWIN,
J. K. SMITH.