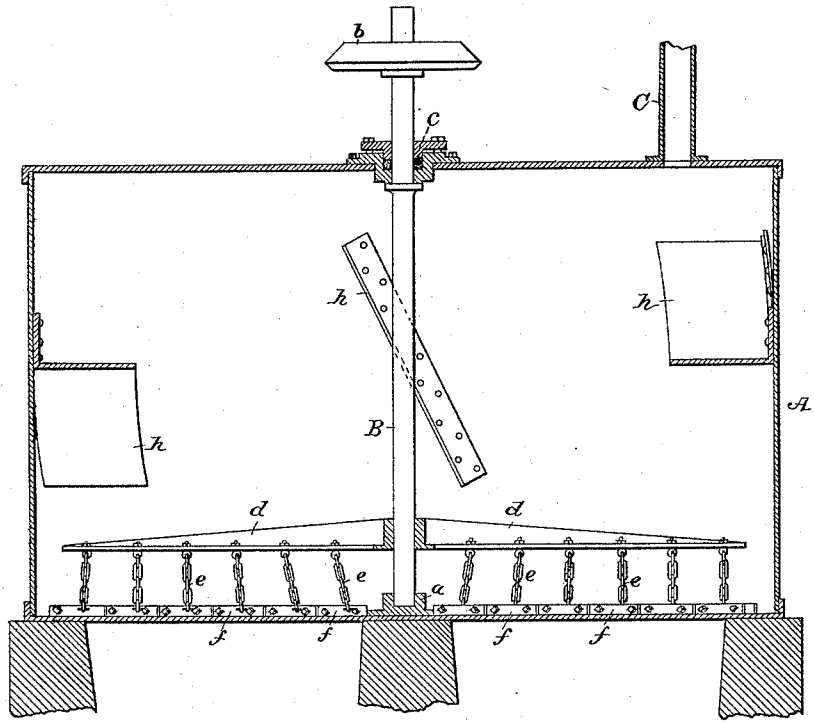
(No Model.)

H. FRASCH.

PURIFYING PETROLEUM.

No. 487,216. Patented Nov. 29, 1892.



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UNITED STATES PATENT OFFICE.

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PURIFYING PETROLEUM.

SPECIFICATION forming part of Letters Patent No. 487,216, dated November 29, 1892.

Application filed December 10, 1888. Serial No. 293,162. (No model.)

To all whom it may concern:

Be it known that I, HERMAN 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 Purifying Petroleum of the Canadian and Lima Class, of which the following specification is a full, clear, and exact description.

This invention relates to the treatment of Canadian and similar petroleum—such, for example, as that found at Lima, in Ohio. This oil requires a different treatment from the ordinary American oil, because of the sulphur compounds which it contains and which give it its penetrating disagreeable odor and render unfit for use unless deodorized. The sulphur is present in these oils in considerable proportions—say upward of one-half of one per cent., (½ of 1%)—mostly in chemical combination, and some, at least, of the sulphur-containing compounds are essentially different from the sulphur compounds which occur in other oils—as, for example, in coal or shale oils—and are retained with great tenacity. The large proportion of sulphur will generally distinguish these from other petroleum; but a further distinction may be found in the nature of the sulphur-containing bodies—namely, that they or some of them give the oils the property of dissolving oxide of lead (lithrage) or may be converted by ordinary distillation, for example, into bodies which impart that property to the oils. To deprive these oils of the sulphur and other injurious compounds is the object of the present invention.

Heretofore it has been customary in Canadian refineries (and the same has been employed in parts of the United States) to take the burning-oil distillate, which has been subjected to the action of sulphuric acid and washed with water, and to treat the same with a solution of plumbate of soda in order to deodorize it and then to add sulphur in powder in order to restore the color, which the plumbate solution has turned to a yellow or brown, and cause the quick precipitation of the lead, leaving the oil above it white and clear. The solution of the soda settles to the bottom. Before adding the sulphur it is customary to remove a small portion of the oil under treatment, and after sulphuring down this portion—that is, after throwing down the lead sulphide by addition of sulphur—to test it with fresh plumbate solution. If it remains unchanged, it is considered that sufficient of the plumbate solution has been added to the main body of oil, and the workman then adds the sulphur to it; but if the small portion tested is changed more of the plumbate solution is added to the main body until a removed portion will stand the test. The objections to this deodorizing process are twofold: first, an excess of sulphur is liable to be added in the second stage, which is injurious to the oil; and, second, the treatment is not thorough, for if the oil be distilled after it has been so treated as to stand the test with or without sulphuring down the distillate will not stand the test, but will be discolored by the addition of the plumbate-of-soda solution.

In my patent, No. 378,246, dated February 21, 1888, I have described and claimed a process not open to these objections for refining or purifying these so-called "Canadian" or "Lima" oils by distilling the same with suitable oxides or compounds mixed with or dissolved in the oil.

The present invention is, as it were, a supplement to or complement of that process.

I have discovered that the refractory sulphur compounds in petroleum of the Canadian or Lima class, which compounds are known to workers in such petroleum as "skunk," can be decomposed by distilling the skunk-bearing oil and subjecting the same to the action within the oil undergoing distillation of the salts of those metals which are precipitated by hydrogen sulphide in acid solution—as the manganates, chromates, borates, sulphates, carbonates, and the like.

The result is that the sulphur compounds in the oil and the salts are mutually decomposed, (or the salts are otherwise decomposed and the constituents thereof attack the sulphur compounds,) with the formation of metallic sulphur compounds and, it may be, other solid bodies or residues, which precipitate and of volatile bodies or residues of the sulphur compounds in the oil, and, it may be, of the acid of the salts also, which pass off

with the petroleum vapors to the condenser. Material may also remain in solution in the liquid residuum in the still at the end of the operation. The metal which is precipitated in combination with sulphur may be derived from the basic or the acid portion of the salt, or from both. The liquid from the condenser will contain some of the volatile products or residues, and it can be further purified by washing with sulphuric acid and then with water and afterward neutralizing. Other treatment to neutralize or remove any broken-down residues of the acid of the metallic salt should such be present can be employed when it may be deemed necessary or desirable. The purified oil may be used for burning or other purpose to which it is or may be applicable.

It is preferred to treat distillates—that is, products which have previously been distilled—and it is specially designed to treat kerosene or burning oil distillates; but crude petroleum or any petroleum product which can be vaporized or distilled may be treated, and the invention extends to the treatment thereof, as well as to the treatment of the burning-oil distillates. I may use the metallic salts alone or I may also use other suitable purifying agents in connection with the metallic salts. I may use one salt or two or more salts and I may use single or double salts. The salts whose acid residues are not volatile, but remain behind with the basic metal in the oil—such as, for example, chromates, which as a result of a treatment are converted into sulphur compounds of the metals and chromic oxide, manganates, which form sulphur compounds of both the acid and basic metals, together, ordinarily, with oxides thereof, and borates, which form sulphur compounds of the metal and boracic acid or biborates of the metal—have the advantage that the salts may be reformed from the residues without the use of additional acid; but it is possible to employ salts whose acid residues are volatile—such, for example, as the sulphates and carbonates—or in which the acid dissolves in the oil.

In carrying out the invention I may employ any suitable apparatus. I have, however, shown in the accompanying drawing a form of apparatus suited to carry into effect the present invention, which latter is not limited to use of this or of any particular form and does not relate thereto, except as the same may be employed in the present improvement in the art, claims to the apparatus being made in the appropriate application based thereon.

The drawing is a vertical section of a still with agitator.

Referring to the drawing, A is a cylindrical iron still which is designed to be heated by a furnace and, except as hereinafter described, is constructed in the usual manner. In the center of the still is a vertical shaft B, the lower end of which rests in a step *a* on the bottom of the still, and to the upper end of which is keyed a bevel-wheel *b* or band-wheel or other gearing, by which a rotary motion is communicated to the shaft B. The top of the still is furnished with a stuffing-box *c*, through which the revolving shaft passes, to prevent the escape at that point of the vapors of distillation which pass from the still through the goose-neck C. The shaft B has attached to it two or more horizontal arms *d*, placed near the bottom of the still and parallel therewith. To these arms *d* are flexibly attached by short chains *e* a number of drags *f*, which may consist of frames composed of two short bars connected by bars at right angles thereto. The function of these drags is to sweep over or scrape the bottom of the still and cause the undissolved salts or material to be thoroughly stirred up and mixed with the oil, and also to prevent the deposit of precipitated sulphides from accumulating as a sediment and burning the bottom of the still. As it is an important matter to preserve the condition of supersaturation of the oil, wings or deflctors *h h* are attached to the inside of the still at convenient distances apart around its periphery. These wings or deflectors (made of metal) are bolted at one side to the still and the other side projects toward the center of the still, but in an inclined position. The effect of these wings or deflectors is to give an upward tendency to the particles of undissolved material when agitated by the stirrer and to effect their more thorough dispersion and suspension in the oil. In place of the bars the drags may consist of chains attached to the arms *d* of the agitator and allowed to hang loosely on the floor of the still, so as to be dragged over its surface as the shaft B and its arms *d* revolve, and other changes in form and construction of the drags will suggest themselves to those skilled in the art. Motion may be communicated to the shaft B in any desired manner.

In operation the still A is supplied with the charge of oil and metallic salt or salts, with or without auxiliary agents—such as rosin or other acid hydrocarbon and plaster or other diffusing material—and distillation is proceeded with, while the agitator in the still is kept in motion, so as to maintain the undissolved salt or salts and other undissolved material in suspension in the liquid. The purifying material may be macerated in the liquid before distillation begins. The vapors pass off from the still to the condenser, (not shown,) where they are reduced to a liquid, which may be further purified by washing with sulphuric acid and water. This operation need not be particularly described, as it is common in other connections in oil-refineries.

A suitable charge for the still would be one hundred (100) barrels of burning-oil distillate, (assuming that the still was of a size ordinarily employed for distilling a charge of that quantity,) of which, say, fifteen per centum (15%) may be heavy oil and four thousand pounds of chromate of lead, or of manganate

of lead, or of borate of lead, or of borate of copper, or of two or more of them, with or without three barrels of rosin and with or without one thousand pounds of plaster-of-paris or similar material. When the burning oil has all been distilled off, the heavy liquid, with the matters in solution and suspension therein, is drawn off, and the solid matter, being strained from the liquid, can have the decomposed or spent portions thereof revivified by roasting and oxidation in a suitable furnace. The liquid can be returned to the still with a fresh quantity of burning-oil distillate.

Other of the decomposable salts could be used instead of or in connection with those specified.

The total quantity may be as given above, which is in excess of the chemical equivalent necessary to bind the sulphur present in the oil.

In the case of the carbonates which are more active than those specified two thousand pounds would suffice for the same quantity of oil.

If the acid residue of the salt or salts used is not a solid, the metallic sulphur compound which collects in the still can be roasted and oxidated and reused with or without supplying additional acid thereto.

The proportions, dimensions, and other details given are set forth by way of example and illustration, and not for the purpose of restricting the invention thereto.

In claiming the salts I would be understood as claiming, also, the revivified residues.

In my concurrent application, Serial No. 378,818, filed January 23, 1891, I have claimed the removal of the sulphur compounds termed "skunk" from Canadian and similar petroleum by vaporizing the oil and subjecting the vapors after they have been given off from the body of the oil to the action of one or more specified metallic oxides, including the decomposable compounds of such oxides, (among which compounds are the metallic salts herein specified,) and in my concurrent application, Serial No. 264,131, filed February 15, 1888, I have claimed the removal of skunk by vaporizing the skunk-bearing oil and subjecting the vapors after they have been given off from the body of the oil to the action of an oily or resinous liquid holding in solution or solution and suspension one or more specified metallic oxides, including the decomposable compounds of such oxides, (among which compounds are the salts herein specified.) In my last-mentioned application I have further claimed vaporizing the skunk-bearing oil and subjecting the same to the action of purifying agents as follows, namely: in one clause to the action of purifying material composed of or containing one or more specified metallic oxides, including the decomposable compounds of such oxides and one or more fatty or resinous acids, and in another clause to the action of a suitable metallic oleate, colophonate, or other metallic salt of a fatty or resinous acid, the expression "vaporizing the oil and subjecting the same to the action of" being intended to apply in each of these clauses as well to the action which occurs within the oil when the latter is distilled with the purifying agent dissolved therein or mixed therewith as to an action on the oil vapors after they have been given off from the body of the liquid oil undergoing distillation. In my application, Serial No. 293,163, filed December 10, 1888, I have claimed cetain treatment of the liquid oil, which treatment does not involve distillation as essential thereto.

I claim herein as my invention or discovery—

1. The process of purifying petroleum of the Canadian and Lima class by distilling the said skunk-bearing petroleum and subjecting the same to the action within the oil undergoing distillation of the salts of those metals which are precipitable by hydrogen sulphide in acid solution, as the manganates, chromates, borates, sulphates, carbonates, and the like, substantially as described.

2. The process of purifying petroleum of the Canadian and Lima class by distilling said skunk-bearing petroleum and subjecting the same to the action within the oil undergoing distillation of the salts of those metals which are precipitable by hydrogen sulphide in acid solutions and which have non-volatile acid radicals or residues, substantially as described.

In testimony whereof I have signed this specification in the presence of two witnesses.

HERMAN FRASCH.

Witnesses:
F. W. LOTHMAN,
WM. V. KEEGAN.