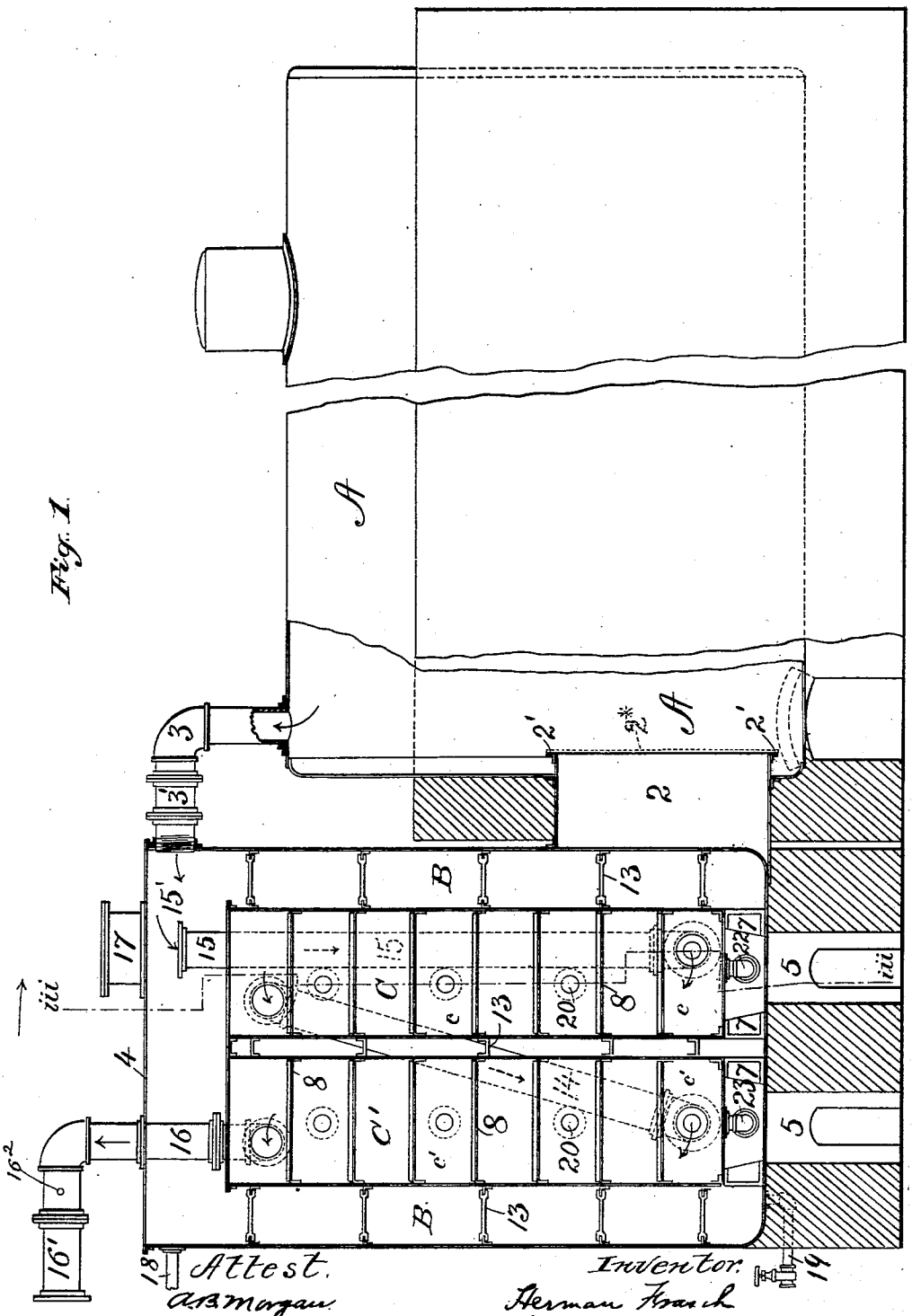
(No Model.) 3 Sheets—Sheet 1.

H. FRASCH.

PROCESS OF AND APPARATUS FOR REFINING LIMA OR SIMILAR PETROLEUM.

No. 564,922. Patented July 28, 1896.

Fig. 1.



(No Model.) 3 Sheets—Sheet 2.

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No. 564,922. Patented July 28, 1896.

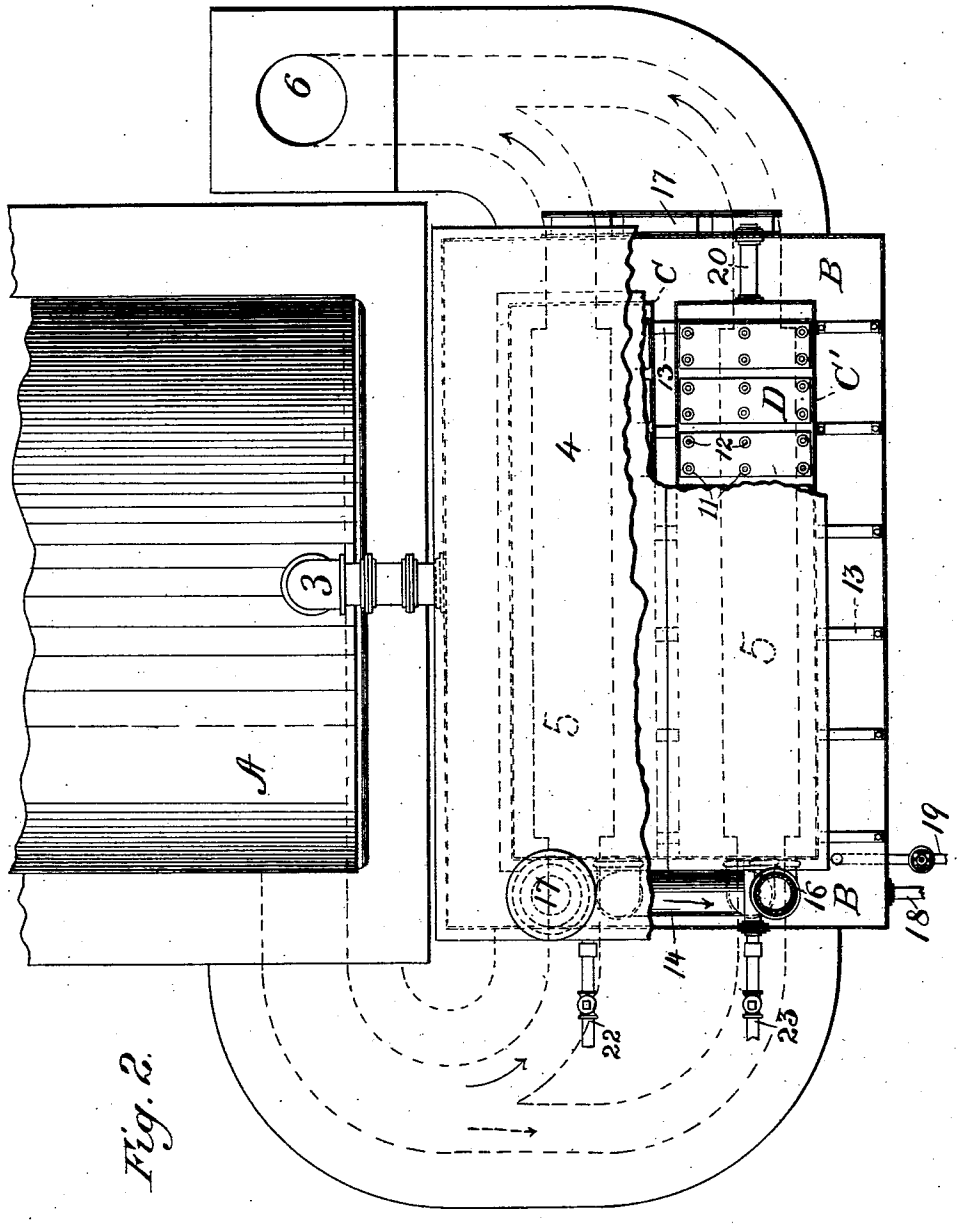

Fig. 2.

Attest:
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W. R. Edelen

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by Chas. J. Hedrick
his attorney

(No Model.) 3 Sheets—Sheet 3.

H. FRASCH.

PROCESS OF AND APPARATUS FOR REFINING LIMA OR SIMILAR PETROLEUM.

No. 564,922. Patented July 28, 1896.

Fig. 3.

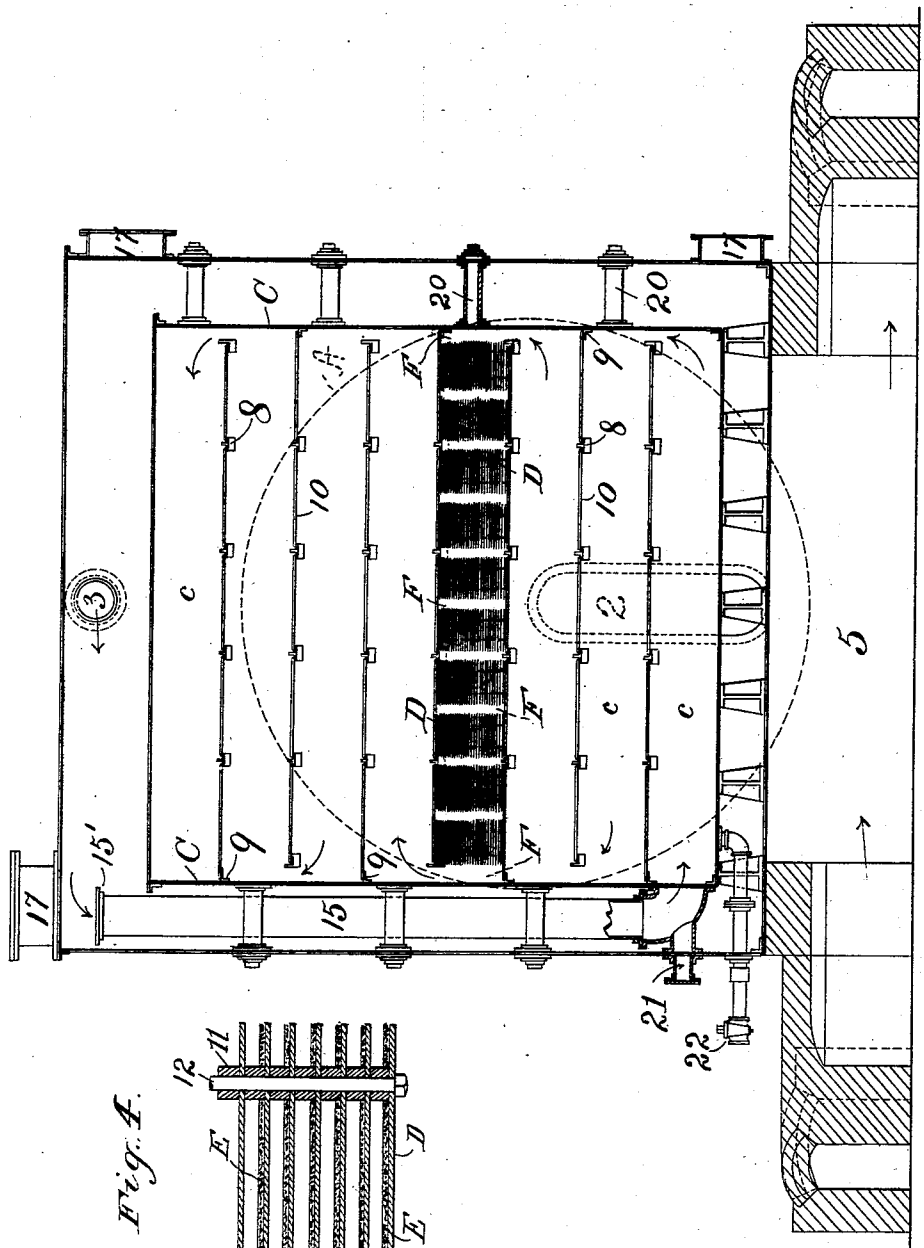

Fig. 4.

Attest.
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W. R. Edelen

Inventor
Herman Frasch
by Chas. J. Hedrick
his attorney

UNITED STATES PATENT OFFICE.

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

PROCESS OF AND APPARATUS FOR REFINING LIMA OR SIMILAR PETROLEUM.

SPECIFICATION forming part of Letters Patent No. 564,922, dated July 28, 1896.

Application filed December 5, 1894. Serial No. 530,875. (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 Processes of and Apparatus for Refining Lima or Similar Petroleum; and I do declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same, reference being had to the accompanying drawings, and to the letters and figures of reference marked thereon, which form a part of this specification.

This invention relates to the removal from Lima or similar petroleum of what is known as "skunk" among workers in that class of oil, the said skunk resisting removal (as is well known) by the ordinary sulfuric-acid and alkali treatment by which oils of the Pennsylvania class have long been satisfactorily refined; but each part of the invention is of course intended to be secured for all the uses to which it may be applicable.

Skunk-bearing oils are found not only about Lima (whence the name) but also in other parts of Ohio, in Canada, and to a less extent in States of the Union other than Ohio. As they come from the well they contain a very considerable percentage of sulfur, (usually upward of one-half of one per cent.,) have a penetrating disagreeable odor, and dissolve litharge (lead oxid) in considerable proportions, the peculiar odor and the property of dissolving litharge, without the aid of oleic acid, rosin, or other added agent, being believed to be characteristic of them and proving the presence of skunk in the oil. The burning oil distillates from ordinary distillation of skunk-bearing petroleum, (whether given the ordinary sulfuric-acid and alkali treatment or not) have the skunk odor, and dissolve litharge. When tested by the addition of a small quantity of an aqueous solution of plumbate of soda, they turn yellow, provided they have previously been freed from sulfureted hydrogen. Otherwise this latter substance causes a dark or black discoloration. On burning in lamps they give a bad odor and cause a cloud on the chimney and a crust on the wick. There has, however, been long known a process (namely, the plumbate-of-soda process, or, as it is commonly called, the "Canadian treatment") by which the burning oil from Lima petroleum can be deprived of its odor and of the property of dissolving litharge without, however, removing the skunk, for on redistillation of Canadian-treated oil the skunk odor reappears and the distillate from such redistillation dissolves litharge and (if free from sulfureted hydrogen) turns yellow with plumbate-of-soda solution. On burning in lamps, the Canadian-treated oils give a bad odor, cloud the chimney, and crust the wick. By the Canadian treatment, therefore, the skunk is concealed, but not removed. For the purpose of removing the skunk from this class of oils I have heretofore devised a number of processes and apparatus. I discovered, among other things, that the skunk could be made to react with suitable substances having a basis of metal, and could thus be decomposed with the formation of a metallic sulfur compound easily separable from the hydrocarbons, and I further discovered various modes whereby such reaction could be brought about industrially.

I obtained very successful results by distilling the skunk-bearing oil with the decomposing substance dissolved therein, and also by vaporizing the oil and passing the skunk-bearing vapors through or over an oily or resinous liquid holding the substance in solution or solution and suspension therein. Further, I obtained useful results in the decomposition of the skunk by the substance in a solid state instead of in solution in an oily or resinous liquid, the said substance being in the form of a more or less finely-ground powder or in larger pieces or lumps. Prior to my present invention, however, all treatments (so far as I am aware) in which the skunk-decomposing substance was used in a solid state without solution in an oily or resinous liquid had proved much less economical and industrially useful than where the skunk-decomposing substance had been used in oily or resinous solution. As just indicated, I have now accomplished an economy and industrial success by the use of the skunk-de-

composing substance in a solid condition equal to or greater than has been accomplished by the use of such substance in solution.

In accordance with the present invention skunk is decomposed by subjecting the skunk-bearing vapors to a solid skunk-decomposing substance in that special state which results from an expansion or swelling of such substance by change of chemical composition when the effect of such change is not impaired by a compacting pressure or a caking temperature. This substance is defined as "solid" in contradistinction to "liquid," and not as signifying that it is firm, dense, or compact, for the substance in its swelled or expanded state is extremely subdivided and very light in comparison with an equal bulk of the same substance in its ordinary condition. An illustration of this swelling effect is seen when finely-divided copper oxid is exposed in the dry state to the vapors of skunk-bearing oil, and the product resulting from such exposure is burned (in other words oxidized, with elimination of more or less sulfur dioxid) at or below a temperature indicated by a dull redness in the dark, the copper compound being so supported as to give the oil-vapors and air access thereto without raking or similarly disturbing the same. For example, taking copper oxid which had been ground very fine and bolted through a cloth with one hundred meshes to the inch, and placing the same in layers of about an eighth of an inch in thickness, I have found such layers to be of more than double such thickness after an exposure to vapors of skunk-bearing oil and a subsequent burning in the manner just stated. The maximum increase of bulk is not, of course, the same always, as it depends on the density of the substance at starting, and the maximum may not be reached in one turn, (*i. e.*, in one skunk-decomposing operation of as many runs as will sufficiently exhaust the substance followed by one burning of the spent substance under the conditions named,) for I have sometimes found the substance to continue to swell through several turns, (the substance remaining throughout on the same trays or supports.) The explanation which I give to this is that the substance is progressively brought to the desired condition.

Letters Patent No. 500,252 were granted to my assignee June 27, 1893, for a skunk-decomposing material composed of the revivified oxid of copper or like metal in a state of velvety fineness and permeability, so that it would dissolve in skunk-bearing oil more readily than commercial oxid; but such material, while an improvement over the ordinary ground oxid, does not have the oxid in the "swelled" condition of the present invention. Copper oxid in the swelled state has from about a half to a third the weight of an equal bulk of ordinary ground-copper oxide or of the comminuted revivified material of my said patent, (500,252.) In a general way it may be said that ordinary ground-copper oxid weighs about one hundred and forty-five pounds to the cubic foot. and the comminuted revivified material of my said patent about one hundred and twenty pounds to the same volume, while an equal bulk of the swelled copper oxid weighs from about forty-five to fifty pounds. Handling tends to bring the particles closer together and thus to impair the swelled condition.

The specific gravity of copper oxid is commonly given at about 6. This would correspond with a weight of about three hundred and seventy-five pounds to the cubic foot. The swelled purificator, composed largely of copper oxid and weighing from forty-five to fifty pounds to the cubic foot, has, therefore, for a given bulk less than a fifth of the weight of copper oxid in a dense non-powdered condition. It may, in fact, be said that the swelled substance has for a given bulk about a fifth or less of the weight corresponding with its common specific gravity.

It must also be understood that it is not necessary to start with a metallic oxid, for the same form of skunk-decomposing substance can be had by starting with other chemical forms, as the sulfid or the sulfate, for example. In the case of sulfid the substance must first be made active, as by burning, because copper sulfid is inactive. With respect to the prepared substance it may be observed that its density would be increased and its efficiency as a skunk-decomposing substance diminished by grinding, as in a mortar, whether followed or not by bolting.

The foregoing illustrations are given in order to enable the principle to be better understood, and not as arbitrarily restricting the invention to such illustrations, although special claims, as particular improvements, are made to the use, or production and use, in the before-mentioned state, of a substance having a basis of copper or like metal, (by which I mean a metal whose oxid is soluble in skunk-bearing oil,) and to the production of a skunk-decomposing substance having a copper or like metallic basis in the beforementioned state, by the specified skunk-decomposition and burning, and to the use of the so-produced substance in further skunk-decomposition.

Further, in accordance with the present invention, the skunk-decomposing substance, as often as it becomes inactive by conversion into a metallic sulfur compound, is revivified on the same supports whereon it is during the prior or subsequent skunk-decomposing operation under conditions favorable to the retention of its peculiar state, as before mentioned.

The skunk-decomposing substance is, of course, originally in a dense form and not swelled; but by the passage over it of the heated-oil vapors it assumes an increased volume and an inactive condition, becoming

charged with sulfur from the said oil-vapors; and by the passage of air a combustion or oxidation of the metal and sulfur ensues which (being performed under appropriate conditions of temperature and pressure) leaves the substance with an enlarged volume and in an active condition, better adapted than originally to induce skunk-decomposition. By effecting the revivification *in situ* the same substance can be used over and over again without renewal or hardening, (which would impair its swelled condition,) and thus by the repeated passage of skunk-bearing vapors and of air a continuous process is secured. The skunk-decomposing substance might be prepared in the swelled state before placing it in the apparatus in which it is to be regularly employed; but by supplying it originally in the ordinary or dense form and first inducing the swelled or expanded condition after it is placed in such apparatus, all necessity of handling it in the swelled state is avoided.

An efficient mode of supporting the skunk-decomposing substance is to place it in layers on trays, which are then made into piles, leaving a passage over the purificator, between the same and the under side of the next tray above. These piles of trays are placed in a duct for the passage of the vapors from the still, leaving a chamber between each pile and the pile following, and thus the numerous passages between trays of each pile all communicate with the chambers on both sides of that pile. The trays in each pile may be upheld and separated by separators placed between adjacent trays, by legs or the like belonging to each tray and resting against another tray, by brackets or the like on (say) the walls of the duct, or otherwise. The arrangement, whether with one or a series of successive piles of trays, forms part of the invention for use in the process before indicated or other uses. In charging the trays for use in such process with powdered skunk-decomposing substance in a dense condition the layers may be each about an eighth of an inch thick, and the space between the trays should be sufficient to permit expansion, leaving free spaces above the expanded layers.

For skunk removal the purifier, consisting of the vapor-duct with one or a series of piles of trays therein, is combined with an oil-still by having the inlet end of the duct connected with the vapor-space of the still and with means (preferably the new or improved means hereinafter specified) whereby the purifier is kept at a temperature to prevent condensation of the vapors from the oil-still. Such combination constitutes a part of the invention.

The invention also includes the improvement in removing skunk from Lima or other skunk-bearing petroleum by passing the volume of vapors (given off from the body of the oil in distillation) in numerous small streams, flowing in a horizontal or inclined direction, over corresponding layers of finely-divided skunk-decomposing substance, or a purificator containing the same, so supported as to leave free passages for the vapors, and revivifying the said substance by similarly dividing the air or other gaseous revivifying agent or agents into many horizontally-flowing parallel streams and passing such streams over the layers, the revivified substance being left in a finely-divided state.

The invention also consists in the features, improvements, constructions, arrangements, and combinations hereinafter specified.

In the accompanying drawings an apparatus is illustrated which is considered the most suitable for carrying the new process or processes of the present invention into effect, and which itself embodies new constructions, arrangements, or combinations, forming a part of said invention.

Figure 1 is a side view or elevation of such apparatus, partly in section, with a middle portion of the still taken out in order to get the figure on the sheet. Fig. 2 is a partial plan of the same, partly broken away to illustrate the construction in horizontal section. Fig. 3 is a vertical section on line *i i i* of Fig. 1, and Fig. 4 is a detail view.

The still A is shown as a cylinder-still of ordinary construction, except for the pipe connections with the chamber B, which forms the jacket of the purifier-boxes C C′. This chamber or jacket communicates at the bottom, through the large pipe 2, with the liquid space, and at the top, through the pipe 3, with the vapor space of the still; so that during a run the oil stands at the same level in the said chamber or jacket as in the still. The cover 4 closes the top of the chamber vapor-tight. The object of this arrangement is to maintain the temperature of the purifier through the medium of the oil in the still. It possesses advantages over an arrangement for heating the purifier through an ordinary sand or liquid bath, or the like, or by direct exposure to a fire or to fire-gases, (whether from a separate fire or the fire under the still,) because if the temperature is maintained by the oil in distillation the purifier-boxes cannot get much hotter than the vapors, never enough so as to injure them by overheating. As distillation proceeds the boxes are raised to a higher and higher temperature, automatically, without care on the part of the attendant. To maintain the temperature of the purifier by means of the liquid oil also possesses advantages over an arrangement for utilizing the vapors for that purpose, because the temperature of the liquid oil is high enough to prevent condensation, which would be detrimental to the skunk-decomposing operation, and even more so to a revivification of the skunk-decomposing substance within the purifier.

It is not essential in order to use other features of invention that the temperature of the purifier be maintained by the heated oil, for,

as to these, the purifier might be kept hot by any ordinary or suitable arrangement, such as a separate fire, or the fire-gases from under the still, applied directly or through an ordinary sand or liquid bath. Neither is it essential to other features that the temperature of the purifier should be gradually raised as the distillation proceeds, for it might be kept at a constant high temperature during a part, and, if the range of gravities be not too great, during the whole of a run without burning the lighter vapors, provided due care be exercised; but it is a special advantage and improvement to have the purifier's temperature rise gradually with the progress of the distillation, keeping above the temperature in the vapor-space of the still, because it insures on the one hand against liquefaction of oil-vapors in the purifier and on the other against overheating of the vapors. In order to secure this, the purifier may advantageously be heated by a liquid whose boiling-point increases with the progress of the distillation, and it is best to use the oil in distillation as such heating medium, because, as already suggested, it dispenses with the need of care on the part of the attendant, since the temperature then regulates itself automatically without permitting of condensation. It will be observed that, as shown, the purifier-boxes are not fully immersed in the liquid oil. This is not material, for the temperature of the portion above the liquid oil (which portion increases as the level of the oil lowers) will also be maintained by the liquid oil, because the latter imparts its heat to the vapors within the immersed portion and the vapors convey the heat to the projecting portion of the purifier.

Underneath the chamber or jacket B are flues 5, (see Fig. 2,) conveying the products of combustion from the space beneath the still to the chimney, whose position is shown at 6. They supply heat to keep up the temperature of the jacketing fluid. The maintenance of the purifier's temperature by the liquid oil could be secured by having the purifier within the still instead of within a communicating chamber, but the use of the latter and the application thereto of heating means outside of the still (to wit, the flues 5) are improvements over an arrangement of the purifier within the still.

The purifier-boxes C C′ rest on supports 7, which in turn rest on the bottom of the jacketing-chamber B. Two of these boxes are shown, but the number is not essential. Within each box are supports (to wit, cross-bars 8 and brackets 9) for supporting the floor-plates 10, by which the box is divided into a series of chambers *c c′*, respectively. The chambers of each series (*c* or *c′*) are so connected as to form a vapor-duct respectively rising in a zigzag fashion from the bottom of the box. At each end of the box every other floor terminates at a distance from the end wall of the box, so as to make the duct run back and forth, lengthwise of the box. On the several floors are piles of many trays D, charged with the skunk-decomposing substance.

If a substance having a basis of copper is used, as is preferred, black oxid of copper from any convenient source, ground, say fine enough to pass through a bolting-cloth having one hundred meshes to the inch, will answer; but it is better to use copper oxide resulting from carefully revivifying the residue from using an oily solution of copper oxid in a skunk-removing operation. Finely-ground copper sulfid or sulfate can be used. Precipitated copper compounds, as sulfid or hydroxid, (or the more or less dehydrated hydroxid,) can be used. The mention of these is not, of course, intended to exclude the use of other forms. A layer E of the substance about an eighth of an inch thick is placed on each tray. The trays are shown as held apart by separators in the form of sleeves 11, Fig. 4, above and below, so as to form passages over the skunk-decomposing substance E. Bolts 12 pass through the trays D and sleeves 11 and clamp the charged trays of each pile together. The piles of trays are separated from one another and the two end walls of the boxes by spaces F, forming the chambers in the duct. The tops of the boxes C C′ are removable, and the floor-plates and piles of trays are introduced through the top. First the bottom is supplied with piles of charged trays, (the same as indicated on the third floor above, in Fig. 3 of the drawings.) Then the floor-plates and piles of charged trays of the floor next above are introduced, and then those of higher and higher floors. Finally the top is put on. This construction of the purifier, with floor plates or trays inserted from the top, is a special improvement; but other suitable constructions could be used in carrying other portions of the invention into effect. The trays might be inclined instead of horizontal, if preferred.

The purifier-boxes C C′ are fastened to each other and to the walls of the chamber or jacket B by stays 13. The top of the vapor-duct in box C is connected with the bottom of the vapor-duct in box C′ by means of the pipe 14. The pipe 15 leads from the vapor-space of the chamber B to the vapor-duct at the bottom of box C, and the pipe 16 from the vapor-duct at top of box C′ to the condenser. (Not shown.) The pipe 15 might of course lead from the vapor-space of the still A. In either case it would receive the vapors from both the still A and chamber B.

The vapor-pipes 3 and 16, as shown, are severally provided with a removable section 3′ and 16′, respectively, for breaking the still and condenser connections when desired. A plate (indicated in dotted lines at $2^{\times}$ in Fig. 1) may be bolted to the flange 2′, so as to close the inlet of pipe 2 whenever it is desired to cut the chamber B off from the still A. A similar plate may be bolted to the flange 15′ when it is desired to close the pipe 15. The

chamber B is further provided with manholes 17, with a water-supply pipe 18, and a draw-off 19.

The boxes C C′ have air-inlet pipes 20 and 21, extending through the jacket B to the outside. There is one of these pipes for each floor. It can be closed with a removable plate or plug, and when open can (if necessary) have the inlet-openings adjusted by means of perforated plates, or reducers, or the like. The boxes also have each a draw-off 22 and 23, respectively, with a stop-cock therein, as shown, for the box C in Fig. 3. In case oil should leak into the boxes the draw-offs serve to remove it; but it is intended to have the boxes tight. The boxes C C′, being charged with the skunk-decomposing substance in an active condition, (say copper oxid,) thinly disposed on its supports, (to wit, the trays D,) are closed, and are put into communication with the still A by the pipes 3 and 15 and with the condenser (not shown) by the pipe 16. The jacketing-chamber B is also put in communication with the still through the pipes 2 and 3. The water-pipe 18, the draw-off 19, the air-inlet pipes 20 and 21, and the draw-offs 22 and 23 are all closed.

The still A is filled to the usual level with, say, crude Lima oil, either containing the naphtha or from which the naphtha has been separated. It might be supplied with distillate, either burning oil or naphtha or other distillate, but crude oil is preferable. The oil flows through the pipe 2 into the chamber B and stands therein at the same level as in the still. The fire is started under the still and the oil heated to the distilling temperature. The skunk-bearing vapors pass by the pipe 15 into the chamber *c* at the bottom of box C. Here, and in the duct above each floor 10, the volume of vapors is divided into numerous small streams, flowing in the same horizontal direction, between adjacent trays D, over the corresponding thin layers of finely-divided skunk-decomposing substance, maintained by the oil at a temperature to prevent condensation without danger of overheating the vapors. At each pile of trays the vapors are divided. The skunk reacts with the substance, forming a metallic sulfur compound which remains on the trays. Other products of the reaction pass off with the oil-vapors. In the chambers F in the duct the vapors of the different streams have an opportunity to mingle before they are divided again into small streams by the next pile of trays. After traversing the several chambers *c* of the tortuous vapor-duct and passing through the piles of trays the vapors reach the top of box C and pass by the pipe 14 to the first chamber *c′* of the vapor-duct in box C′ at the bottom of said box. They pass up through such duct, being divided repeatedly into numerous small parallel streams flowing horizontally over the thin layers of skunk-decomposing substance, and they escape, with the volatile products of the skunk-decomposition, by the pipe 16 to the condenser. They are thereby reduced to a liquid, which may be subjected to any further operation which may be desired. The burning-oil fraction would be finished by the well-known sulfuric acid and alkali treatment. The naphtha (if not previously removed, as it preferably would not be) would also have its skunk decomposed and would be finished in the usual way.

During the distillation lighter vapors of course first pass off and then the heavier vapors, and the heavier the vapors the higher becomes the temperature in the still A, chamber B, and purifier-boxes C C′. The vapors generated in still A enter the jacket B by the pipe 3, and pass with the vapors from the oil therein into the purifier-boxes C C′ by the pipe 15. The distillation would ordinarily be stopped and the residuum drawn off after the removal of the burning oil, although heavier fractions could be freed from skunk in accordance with the invention,

After the skunk-decomposing substance has become sulfured and inactive, or as much so as is thought proper, and at the end of a run, when the residuum has been drawn off from still A and chamber B, the communication of the still and condenser with the purifier and its jacket is cut off by applying a plate (indicated at $2^{\times}$ in Fig. 1) to the flange 2′ over the end of pipe 2 and by removing the pipe-sections 3′ and 16′. The outer end of that portion of pipe 3 which is attached to the jacket B, and also the upper end of pipe 15, is closed, and the outer end of the part of pipe 16 which is attached to the box C′ is left open or is connected, as desired. The chamber B is next supplied with water at ordinary temperature by the pipe 18 to a little below the level of such pipe, after which no further supply of water is necessary, at least under ordinary conditions. One or more of the air-inlet pipes 20 and 21 are opened and a draft is established, as, for example, by an aspirating steam-jet, (indicated at 16^{2}.) The skunk-decomposing substance ignites and burns with an active combustion. Preferably all the air-inlets are left open, so that the combustion is maintained on all floors at the same time. Owing to the thinness with which the skunk-decomposing substance is disposed on its supports, the combustion is readily controllable by regulating, when necessary, the admission of air through the air-inlet pipes and by the cooling effect of the water in the jacket B. The use of adjustable covers or of perforated plates or reducers at the outer end of each branch will serve to regulate the air admissions, or the pipes might have the right bore to be left fully open. The disposition of the skunk-decomposing substance on its supports allows the air access without raking, and the products of combustion pass through the vapor-duct to escape by the pipe 16.

A practical test is so to adjust the air admission that the combustion goes on actively enough to boil the water in the jacket B vig-

orously, without going beyond the production of a dull redness in the dark, as seen through the air-inlet at the early part of the operation. Such glow would soon disappear, and it is not necessary for it to appear even in the early part of the combustion. With a proper air admission the proper sulfur compound burns without flame, and is soon converted into a mixture (in greater or less proportions) of copper sulfate and copper oxid. Sulfur dioxid is given off and may be detected in the gases from the pipe 16 by its odor. When the water in jacket B ceases to boil, the revivification may be considered complete, the air-inlets closed and the purifier, with its contents, allowed to cool.

For a purifier having a tortuous vapor-duct whose cross-section is three feet wide and seventeen and a half inches high, with ten piles of trays to each floor of the duct, with thirty-six trays to a pile, and with an original eighth-inch layer of ground copper oxid on each tray, one air-inlet pipe may be used for each floor with an inlet-opening two inches in diameter, that diameter of opening being maintained without change throughout the revivification, a quarter-inch jet of steam under ordinary boiler-pressure, say sixty pounds to the square inch, being introduced through a pipe 16^2 at a convenient point into the ten-inch pipe 16. With such air-inlets the temperature will not rise too high if the substance has become fully charged with sulfur, and active combustion will go on satisfactorily when the substance has become sulfured only to a comparatively small extent. For other sizes of purifier the general suggestion is to make the air-inlets larger or smaller as the cross-section of the vapor-duct is greater or less, and the preceding directions will be sufficient explanation for those skilled in the art to carry out the revivification practically.

The advantage of using the liquid oil to maintain the temperature of the skunk-decomposing substance in the skunk-decomposing operation, and thus effectually preventing all condensation of vapors in the purifier, is very manifest in the revivifying operation, because the combustion of condensed oil would be apt to cause a temperature detrimental to the skunk-decomposing substance or to the apparatus or to both.

When the fire goes out for want of fuel, (a condition indicated, as before stated, by the cessation of ebullition of the water in the jacket B,) the skunk-decomposing substance is left chemically active and in whole or in part in the desired state. The layers of such substance will be found to be swollen or expanded considerably beyond their original thickness, and the substance itself to be a more active and efficient agent for decomposing skunk than was the finely-ground oxid of copper originally placed in layers on the trays. Reference is made to a partial conversion of the substance into the desired condition, because, as already mentioned, it may happen that the ground copper oxid does not acquire its maximum volume until after two or more turns, and it is supposed that this is due to the fact that the rearrangement of the atoms or molecules (to which the desired state is attributed) proceeds gradually from the surface of each of the fine particles inward.

After the revivification the apparatus is restored to the first-described state, the still A and jacket B filled with crude oil and one or more additional runs made, until the skunk-decomposing substance is ready for another revivification. If the revivified material is a mixture of oxid and sulfate of copper, sulfur dioxid and water accompany the petroleum vapors to the condenser, which should preferably be lead-lined. The sulfur dioxid or sulfurous acid may be removed and utilized.

So far as I am aware, there is no limit to the number of times which the same charge of substance can be revivified and reused, and my experience leads me to think that the same charge can be used indefinitely.

If the purifier is charged with the skunk-decomposing substance in an inactive condition, (say as copper sulfid,) it is made active (for example, by active combustion, as in the revivification described) before the skunk-bearing vapors are passed over it.

In a number of the claims following reference is made to a non-caking temperature and an absence of compacting pressure. To avoid explanation of the expressions repeatedly in the different claims, it may here be said, once for all, that by "non-caking temperature" is meant one below that which would cause a union or agglomeration of the particles of the skunk-decomposing substance, and that by an "absence of compacting pressure" is meant a freedom from raking, grinding, or other operation sufficient to unite the particles by compression.

I claim as my invention or discovery—

1. The continuous process of removing skunk from Lima or similar petroleum, consisting in exposing a comminuted oxid or salt of copper or like metal to the vapors of such oil and (when the said substance is charged with sulfur) to air so as to revivify the same by oxidation of the metal and sulfur, all under the conditions of a non-caking temperature and an absence of compacting pressure, and then repeating the described operations under said conditions of heat and pressure, without removal of the said substance from the apparatus in which the process is carried on by the passage of skunk-bearing vapors to decompose the skunk and of air to revivify the skunk-decomposing substance, substantially as set forth.

2. The improvement in the art of removing skunk from Lima or similar petroleum, consisting in inducing in a skunk-decomposing substance a swelled or expanded and extremely-subdivided condition by exposure of said substance to skunk-bearing vapors and

to a gaseous revivifying agent under the conditions of a non-caking temperature and an absence of compacting pressure, and subjecting the skunk-bearing vapors to the said substance in its so-obtained swelled or expanded and extremely-subdivided condition, substantially as described.

3. The improvement in the art of removing skunk from Lima or similar petroleum, consisting in so supporting the skunk-decomposing substance as to give aeriform fluid access thereto without raking or similar disturbance, and exposing the so-supported substance in a dry state to skunk-bearing vapors to effect the decomposition of the skunk and to air under the conditions of a non-caking temperature and an absence of compacting pressure induced therein before or after it is placed on its supports; substantially as described.

4. The improvement in the art of removing skunk from Lima or similar petroleum, consisting in inducting in a skunk-decomposing substance having a basis of copper or like metal a swelled or expanded and extremely-subdivided condition by exposure of such substance having a basis of copper or like metal to vapors of skunk-bearing oil and to air under the conditions of a non-caking temperature and an absence of compacting pressure, and subjecting the skunk-bearing vapors to the said substance in its so-obtained swelled or expanded and extremely-subdivided condition, substantially as described.

5. The improvement in the art of removing skunk from Lima or similar petroleum, consisting in subjecting the skunk-bearing vapors to a solid skunk-decomposing substance in the herein-described condition of extreme subdivision; the substance in said condition having for a given bulk from about a half to a third of the weight which it has when in the state of ordinary finely-ground powder, substantially as described.

6. The improvement in the art of removing skunk from Lima or similar petroleum, consisting in subjecting the skunk-bearing vapors to a solid skunk-decomposing substance in the form of a metallic oxid or salt in the herein-described condition of extreme subdivision; the substance in said condition having for a given bulk from about a half to a third of the weight which it has when in the state of ordinary finely-ground powder, substantially as described.

7. The improvement in the art of removing skunk from Lima or similar petroleum, consisting in subjecting the skunk-bearing vapors to an oxid or salt of copper or other metal whose oxid is soluble in skunk-bearing oil in the herein-described condition of extreme subdivision, such oxid or salt having for a given bulk from about a half to a third of the weight of an equal bulk of ordinary finely-ground oxid or salt of copper or like metal, substantially as described.

8. The process of preparing a purificator, consisting in inducing in the skunk-decomposing substance a swelled or expanded and extremely-subdivided condition by exposure of said substance to skunk-bearing vapors and to a gaseous revivifying agent under such conditions of temperature and pressure as favor the retention of a swelled or expanded state, that is to say under the conditions of a non-caking temperature and an absence of compacting pressure, substantially as described.

9. The process of preparing a purificator consisting in inducing in the skunk-decomposing substance a swelled or expanded and extremely-subdivided condition, by exposure of said substance to vapors of skunk-bearing oil and to air under such conditions of temperature and pressure as favor the retention of a swelled or expanded state, that is to say under the conditions of a non-caking temperature and an absence of compacting pressure, substantially as described.

10. The process of preparing a purificator, consisting in inducing in a skunk-decomposing substance having a basis of copper or like metal a swelled or expanded and extremely-subdivided condition, by exposure of said substance having a basis of copper or like metal to vapors of skunk-bearing oil and to air under such conditions of temperature and pressure as favor the retention of a swelled or expanded state, that is to say under the conditions of a non-caking temperature and an absence of compacting pressure, substantially as described.

11. As a new article of manufacture, for use in removing skunk from Lima or similar petroleum, a purificator consisting of a skunk-decomposing substance in the herein-described condition of extreme subdivision, the same having for a given bulk about a half to a third of the weight which it has when in the state of ordinary finely-ground powder, substantially as described.

12. As a new article of manufacture, for use in removing skunk from Lima or similar petroleum, a purificator consisting of a skunk-decomposing substance in the form of a metallic oxid or salt in the herein-described condition of extreme subdivision, the same having for a given bulk from about a half to a third of the weight which it has when in the state of ordinary finely-ground powder, substantially as described.

13. The purificator, consisting of an oxid or salt of copper or other metal whose oxid is soluble in skunk-bearing oil in the herein-described condition of extreme subdivision; as a new article of manufacture for use in removing skunk from Lima or similar petroleum, the said purificator having for a given bulk from about a half to a third of the weight of an equal bulk of ordinary finely-ground oxid or salt of copper or like metal, substantially as described.

14. The improvement in the art of removing skunk from Lima or similar petroleum, con-

sisting in passing the skunk-bearing vapors in numerous horizontally-flowing streams over closely-set layers of skunk-decomposing substance, the passages between the layers being of such relative length and height as that all the skunk is necessarily brought into contact with the said substance, substantially as described.

15. The improvement in the art of removing skunk from Lima or similar petroleum by a continuous process, consisting in passing the skunk-bearing vapors in small horizontally-flowing streams over layers of a finely-divided skunk-decomposing substance, and revivifying such substance by passing over said layers similar streams of a gaseous revivifying agent so as to leave the said substance in a finely-divided condition for repeated action, substantially as described.

16. The improvement in the art of removing skunk from Lima or similar petroleum, consisting in supporting the skunk-decomposing substance in a solid finely-divided state in a way to give access of an aeriform fluid thereto without raking or similarly disturbing the substance, passing the skunk-bearing vapors over the so-supported substance when it is in the active condition, and effecting revivification by an active combustion of the so-supported spent substance which oxids both the sulfur and the metal and leaves the revivified substance in a solid finely-divided condition, substantially as described.

17. The method of revivifying a skunk-decomposing substance having a basis of copper or like metal, by producing an active combustion of the sulfured substance while so supported as to give the air access thereto without raking or similar disturbance, and controlling such combustion so as to maintain a non-caking temperature, substantially as described.

18. The method of revivifying a skunk-decomposing substance having a basis of copper or like metal, by producing an active combustion of the sulfured substance while so supported as to give the air access thereto without raking or similar disturbance, and controlling such combustion below the point of decomposition of the sulfate of the metal constituting the basis of such substance so as to retain a substantial proportion of such metallic sulfate in the revivified substance, substantially as described.

19. The method of revivifying with active combustion a skunk-decomposing substance having a basis of copper or like metal, by having the said substance thinly disposed on the supports whereon it is held in burning, absorbing excess of heat by a cooling medium, and adjusting the air supply, so that active combustion goes on at a non-caking temperature, substantially as described.

20. The method of revivification, consisting in producing an active combustion of the sulfured substance while so supported as to give the air access thereto without raking or similar disturbance, and controlling such combustion by the aid of a cooling medium at a temperature indicated by dull redness or blackness, substantially as described.

21. The method of revivification, consisting in producing an active combustion of the sulfured substance while so supported as to give the air access thereto without raking or similar disturbance, and controlling such combustion by the aid of an immersion of the combustion-chamber in a cooling liquid at a temperature indicated by dull redness or blackness, substantially as described.

22. The improvement in the art of removing skunk from Lima or similar petroleum, consisting in vaporizing the oil, and subjecting the vapors to a skunk-decomposing substance in a solid finely-divided condition whose temperature is raised gradually with the progress of distillation by means of a liquid of variable boiling-point corresponding with the varying temperature in the vapor-space of the still and slightly above such latter temperature, substantially as described.

23. The improvement in the art of removing skunk from Lima or similar petroleum, consisting in vaporizing the oil, and subjecting the vapors to a solid finely-divided skunk-decomposing substance whose temperature is kept above that of the vapor-space of the still by means of a vaporizable liquid of a boiling-point higher than the temperature of said vapor-space and below the point of decomposition of the vaporized hydrocarbons from said space, substantially as described.

24. The improvement in the art of removing skunk from Lima or similar petroleum, consisting in vaporizing the oil, and subjecting the vapors to a skunk-decomposing substance in a solid finely-divided condition whose temperature is maintained by the heated oil in distillation, substantially as described.

25. The improvement in the art of removing skunk from Lima or similar petroleum, consisting in vaporizing the oil, subjecting the vapors to a skunk-decomposing substance in a solid finely-divided condition, whose temperature is maintained by the heated oil in distillation, and revivifying the said substance by combustion on the supports whereon it is used leaving the same in a solid finely-divided condition, substantially as described.

26. An oil-still provided with a purifier having its inlet in communication with the vapor-space of the still and its outlet leading to a condenser, the said purifier being exposed externally to fluid of the still and having a duct for the oil-vapors arranged to be heated by the liquid oil, substantially as described.

27. An oil-still provided with a purifier having a jacketing-chamber in communication with the liquid space of said still, said purifier being connected with the vapor-space of said still and having an outlet leading to a condenser, substantially as described.

28. The combination with an oil-still, of a

jacketed purifier having its jacket connected with the interior of the still, and means outside the still for heating said jacket externally, substantially as described.

29. In combination with an oil-still, a purifier exposed externally to the oil in distillation and having its inlet connected with the vapor-space of said still and its outlet leading to a condenser, means whereby said connection can be broken, means for admitting air into said purifier, and means for supplying a cooling medium to the outside of said purifier, substantially as described.

30. In combination with an oil-still, a jacketed purifier having its jacket connected with the interior of the still and the inlet to the purifier in communication with the vapor-space of the still and the outlet leading to a condenser, means whereby said connection can be broken, means for admitting air into the purifier, and means for supplying a cooling medium to said jacket, substantially as described.

31. A jacketed purifier having a vapor inlet and outlet and provided also with a tortuous vapor-duct, and also with air-inlet pipes opening at the inner ends into said duct at different levels and at their outer ends into the air outside said jacket, substantially as described.

32. An oil-still provided with a purifier exposed externally to the liquid oil, so as to have its temperature maintained by said oil, and having its inlet connected with the vapor-space of the still and its outlet leading to a condenser, substantially as described.

33. An oil-still provided with a purifier exposed externally to the liquid oil, so as to have its temperature maintained by the said oil, and having its inlet connected with the vapor-space of the still and its outlet leading to a condenser, said purifier being further provided with means for admitting air thereinto, substantially as described.

34. In combination with an oil-still, a vapor-duct interposed between the vapor-space of said still and a condenser and exposed externally to the liquid oil, so as to have its temperature maintained by said oil, and one or more piles of trays in said duct with open-ended passages between said trays, substantially as described.

35. In combination with an oil-still, a vapor-duct interposed between the vapor-space of said still and a condenser and exposed externally to the liquid oil, so as to have its temperature maintained by said oil, one or more piles of trays in said duct with open-ended passages between said trays, and means for admitting air to pass through said duct between said trays, substantially as described.

36. In combination with an oil-still, a purifier arranged within an oil-holding space or vessel, so as to have its temperature maintained by the liquid oil, and having its inlet connected with the vapor-space of said still and its outlet leading to a condenser, means whereby the connection may be broken between the said vapor-space and the interior of said purifier, means for admitting air into said purifier, and means for supplying a cooling medium to the first-named space or vessel, substantially as described.

37. A purifier arranged within a liquid-holding space or vessel, so as to have its temperature regulated by the liquid in said space or vessel, in combination with means for delivering vapors into said purifier, and means for admitting air into said purifier, substantially as described.

38. A vapor-duct arranged within a liquid-holding space or vessel, so as to have its temperature regulated by the liquid in said space or vessel, and one or more piles of trays in said duct with open-ended passages between said trays, in combination with means for delivering vapors into said duct, and means for admitting air into said duct, substantially as described.

39. In combination with an oil-still, a vapor-duct interposed between the vapor-space of said still and a condenser, means for heating or maintaining the temperature of said duct, and one or more piles of closely-set trays in said duct with open-ended passages between said trays, the said passages being of such relative length and height as that all particles of the vapors which pass through said duct are suitably exposed to the substance on said trays, substantially as described.

40. In combination with a still, a jacketed purifier having an inlet connected with the vapor-space of the still and a vapor-outlet leading to a condenser and provided also with floors therein so arranged as to form a tortuous vapor-duct, with air-inlet pipes opening at the inner ends into said duct at different levels and at their outer ends into the air outside the said jacket, and with pipe connections between the said jacket and the interior of said still, pipe closures and disconnectors being also provided for breaking the connection between the still and the interior of the purifier in revivification and closing the air-inlets in skunk-decomposition, substantially as described.

In testimony whereof I affix my signature in presence of two witnesses.

HERMAN FRASCH.

Witnesses:
HOWARD E. COLE,
F. D. WILLIAMS.

Corrections in Letters Patent No. 564,922.

It is hereby certified that in Letters Patent No. 564,922, granted July 28, 1896, u
the application of Herman Frasch, of Cleveland, Ohio, for an improvement in "Proce
of and Apparatus for Refining Lima or Similar Petroleum," errors appear in
printed specification requiring correction as follows: On page 5, line 104, a com
should be inserted after the word "open;" same page and line the comma after
word "connected" should be stricken out; page 6, line 7, the word "proper" sho
read *copper;* page 7, line 18, after the word "pressure" the clause *so as to favor
retention of the swelled or expanded state of the said substance* should be inserted, and s
page, line 23, the word "inducting" should read *inducing;* and that the said Let
Patent should be read with these corrections therein that the same may confor
the record of the case in the Patent Office.

Signed, countersigned, and sealed this 1st day of September, A. D., 1896.

[SEAL.]

JNO. M. REYNOLDS,
Assistant Secretary of the Interi

Countersigned:

S. T. FISHER,
Acting Commissioner of Patents.