

(No Model.)

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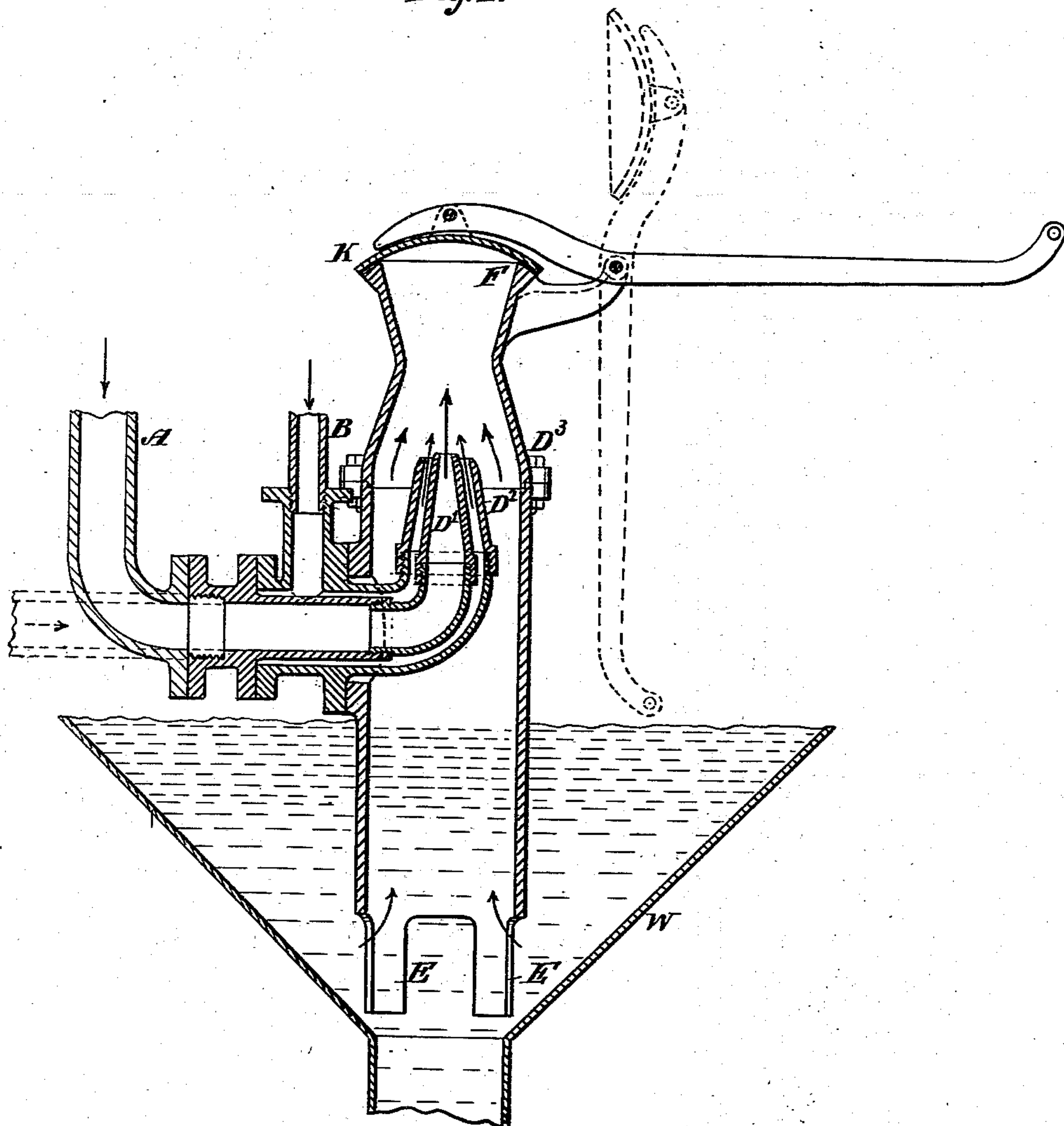
H. WOLF.

PROCESS OF AND APPARATUS FOR REFINING CRUDE PETROLEUM, &c.

No. 604,280.

Patented May 17, 1898.

Fig. 1.



WITNESSES:

E. Wolff
Chas. E. Fournier

INVENTOR:

Hermann Wolf.

BY

Hauff & Hauff
ATTORNEYS.

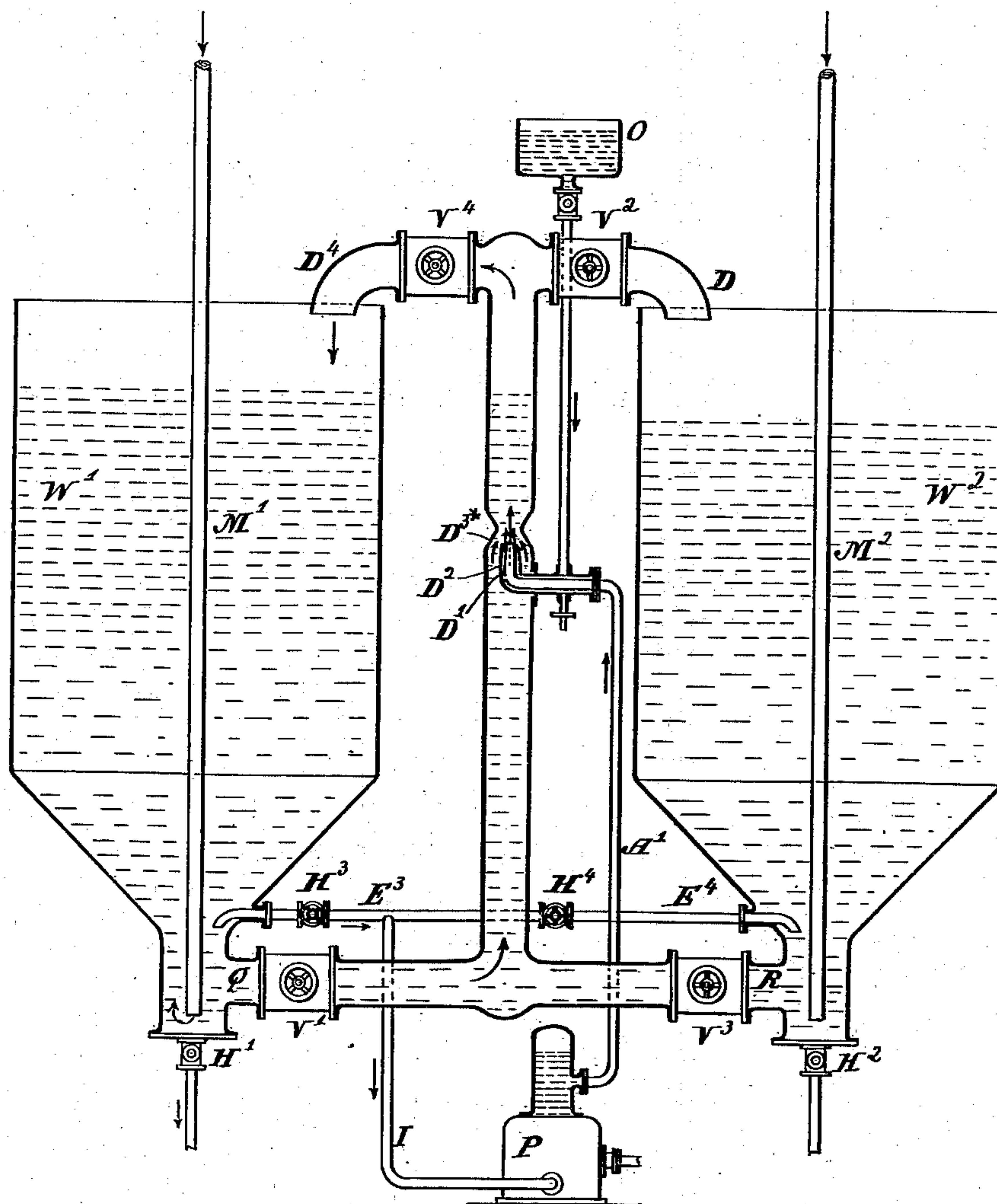
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Fig. 2.



WITNESSES:

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INVENTOR:

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UNITED STATES PATENT OFFICE.

HERMANN WOLF, OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY, ASSIGNOR
TO THE BADISCHE ANILIN AND SODA FABRIK, OF SAME PLACE.

PROCESS OF AND APPARATUS FOR REFINING CRUDE PETROLEUM, &c.

SPECIFICATION forming part of Letters Patent No. 604,280, dated May 17, 1898.

Application filed February 7, 1896. Serial No. 578,441. (No model.) Patented in England December 6, 1895, No. 23,436; in Germany January 28, 1896, Nos. 92,018 and 93,702; in Hungary March 24, 1896, No. 5,954, and in Austria June 10, 1896, No. 46/2,280, and July 2, 1896, No. 46/2,635.

To all whom it may concern:

Be it known that I, HERMANN WOLF, a subject of the Emperor of Austria, residing at Ludwigshafen-on-the-Rhine, in the Kingdom of Bavaria and Empire of Germany, have invented new and useful Improvements in Processes of and Apparatus for Refining Petroleum, (for which Letters Patent were obtained in Great Britain, No. 23,436, dated December 6, 1895; in Austria, No. 46/2,280, dated June 10, 1896, and No. 46/2,635, dated July 2, 1896; in Hungary, No. 5,954, dated March 24, 1896, and in Germany, Nos. 92,018 and 93,702, dated January 28, 1896,) of which the following is a specification.

The general process hitherto used for refining the various fractions of unrefined petroleum and analogous oils—such as the various rock-oils and the oils obtained by distillation of coal-shale and coal-tar—consisted in mixing them with concentrated sulfuric acid, the acid not being in a condition of fine or ultimate subdivision at the time of incorporation with the oil, and subsequent agitation being relied on to subdivide the acid and distribute it through the oil. The acid solution of impurity was then separated and the oil washed with water and alkali. I hereinafter refer to these various oils and their distillates generally as “oils.” More recently attempts have been made to use Nordhausen or fuming sulfuric acid or “oleum,” as it is known in the trade, instead of concentrated sulfuric acid in the same way, but satisfactory results have not been obtained.

I have discovered the causes of failure and have invented improvements whereby the difficulties are overcome and most satisfactory results, better than those hitherto obtained in any way, are achieved.

I have discovered that fuming sulfuric acid immediately on coming into contact with some unrefined oils rapidly forms pitch-like bodies, so that if the mixing be effected in the usual way small drops are formed, each consisting of an outer layer of pitch-like body, but composing an inner nucleus of practically unaltered fuming sulfuric acid, which either takes

no part in the purification or only does so after prolonged agitation. The subdivision of the acid is therefore limited by the formation of these envelopes impervious both to acid and to oil. I have also discovered that this difficulty may be overcome by reducing the acid to a condition of fine subdivision and in this condition thoroughly mixing it with the oil. To accomplish this result, I prefer to introduce the acid at the point of contact of two streams of unrefined oil (or one stream of air or other gas and one of unrefined oil) while the said streams possess a different velocity, so that considerable friction occurs between the streams, whereby the acid is in a sense rubbed or ground into a fine state of division and becomes most intimately admixed with the entire body of unrefined oil.

I have also discovered that another cause of failure is due to the fact that when treating some unrefined oils, especially the heavier fractions, with fuming sulfuric acid, besides the ordinary pitch-like compound of acid impurity which separates out, other similar combinations are formed, in some cases, which do not separate from the oil. If the oil containing such combinations be washed in the usual way with water and alkali without any steps being first taken to remove the said combinations, then the impurities are regenerated and impart a dark color and objectionable smell to the product. I have discovered that the said acid-impurity combinations can readily be removed by treating the oil containing them with a small percentage of sulfuric acid, preferably containing from seventy-five to one hundred per cent. H_2SO_4 .

By working according to this invention the following advantages are obtained: The oil obtained is lighter in color than can be obtained when using either concentrated sulfuric acid alone or fuming sulfuric acid alone. Further, on exposure to light the refined product continuously becomes lighter in color, whereas the product refined with ordinary concentrated acid only bleaches a little at first, but afterward reverts in color, becoming yellow. There is also less oil lost when using

the new refining process, only about half as much pitch-like acid-impurity combination being formed.

It is not always necessary to apply both of the improved means in order to obtain the desired result, as in some cases merely securing the intimate admixture of the fuming sulfuric acid with the unrefined oils leads to a highly-refined product; also, in some cases the after treatment, with a small percentage of concentrated acid after mixture with fuming sulfuric acid in the ordinary way, is sufficient without the application of the special mixing process.

The process can be conveniently described more in detail, together with the apparatus, by reference being made to the accompanying drawings, in which—

Figure 1 shows a section of the apparatus which can be used in carrying out my invention. Fig. 2 is a section of a modification of this apparatus.

The apparatus which is shown in Fig. 1 consists of a cylindrical casing D^3 , into which lead two concentric conical nozzles D' and D^2 . The pipe A for compressed air or for oil under pressure is connected with the inner nozzle D' , and the pipe B for the fuming sulfuric acid ends in the nozzle D^2 . Above the opening of the nozzles the casing is first conically constricted, then expands in the shape of a funnel F, and is provided with a lid K. The lower end of the casing is provided with lateral openings E, through which the unrefined oil enters the casing D^3 . As figured in this drawing, the apparatus is placed at the lowest point of or down into the large tank or vessel W, called the "agitator." The agitator W may extend up about the casing D^3 to any suitable height.

The operation is commenced by forcing compressed air through the pipe A, and so through the inner nozzle D' , into the unrefined oil. Instead of using compressed air a stream of the oil itself can be forced in through A and D' at the pressure of two atmospheres or more. The lid K must be open. This compressed stream of air or oil causes a violent motion of the oil in the apparatus upward from E to F. This stream of oil may be drawn from the supply of oil in the apparatus, or it may be injected into the apparatus from an outside source or supply; but in the latter case care must be taken not to inject such an amount of oil as would cause the apparatus to overflow or to become charged with oil above the desired level. A circulation is thus set up, so that the oil is sucked into the apparatus at E and is hurled upward centrally. The fuming sulfuric acid is allowed to run in through the pipe B and nozzle D^2 . At the moment that it emerges from the nozzle it is caught between the two streams of air and oil, or oil and oil, and by the friction between them it is rubbed into a most fine state of division and passes forward, mixed with the liquids, into the mass

of the oil in the agitator. When the admixture is complete, the lid K is closed.

When it is desired to use compressed air, the lid K should be closed and air forced into the apparatus through A, and the air will stream out of the apparatus at E and will agitate the mixture in a manner similar to that hitherto customary. The pitchy particles of the acid-impurity compounds rapidly ball together, and at the end of this agitation with air rapid settling of the acid pitch-like matter results.

The lid K prevents the acid pitch-like matter from entering into the apparatus and stopping up the nozzles, and, further, the apparatus is everywhere so constructed that all the acid pitchy matter settling upon it readily runs off.

When agitating with oil, the agitator W is only charged with sufficient oil that this stands from three to five feet above the casing D^3 . The oil forced through A and D' under pressure, as aforesaid, is drawn from an outer reservoir or supply or from the charge of oil in the agitator W.

When it is desired to stir for a longer time, some of the mixture is drawn by a pump or suitable appliance out of the agitator W when full and forced in again through the casing D^3 under pressure. The pitchy particles are so finely divided that no difficulty through their choking the apparatus or pump is incurred. The pump should be of cast-iron in all its parts and protected from contact with the air by means of petroleum or oil to prevent rust or corrosion.

After the acid pitch has been run off it is generally advisable, especially with heavy oils, as hereinbefore explained, to treat the product with about one or two per cent. of concentrated sulfuric acid, preferably containing about seventy to one hundred per cent. H_2SO_4 . This can be effected in the same apparatus by running in the concentrated acid through the nozzle D^2 instead of the fuming sulfuric acid with the lid K closed or open, as desired.

I have hitherto stated no proportions and given no figures as to the strength of fuming sulfuric acid to be applied, for these vary considerably, according to the oil treated and the degree of impurity. In general about half as much is used as it was hitherto customary to take of concentrated sulfuric acid, and good results have been obtained by the following proportions, namely: for oils obtained by distillation of coal-shale and coal-tar, twenty to sixty per cent., by weight, of anhydrid; for petroleum, ten to twenty per cent., by weight, of anhydrid; for lubricating-oil, five to twenty per cent., by weight, of anhydrid; for vaseline, twenty-five to thirty per cent., by weight, of anhydrid.

Another arrangement of the apparatus is shown in Fig. 2 of the drawings. The outer casing of the apparatus D^{3*} forms part of a system of pipes between two agitators, through

which the oil circulates, and a lid to the apparatus becomes unnecessary. The pipe, which forms the continuation of the casing, has branches D^4 and D above and Q and R below. All these branches are furnished with valves V^1 , V^2 , V^3 , and V^4 and connect the two agitators W^1 W^2 not only with one another above and below, but also the lower part of each agitator with its upper part, so as to enable oil to be sucked from the bottom of one of the agitators and run into it again at the top. The inner nozzle D^1 is connected by the pipe A^1 with the force and suction pump P . The suction-tube I of this pump has branches E^3 and E^4 , each furnished with a valve H^3 and H^4 and entering the agitators W^1 and W^2 , respectively, at their bottoms. The outer nozzle of the apparatus is connected with the tapped vessel O , containing the fuming sulfuric acid. The agitators are, as usual, furnished with a pipe M^1 and M^2 for compressed air. With this arrangement of apparatus it is possible to work in a manner exactly analogous to that already described. Thus the valves V^1 , V^4 , and H^3 may be opened and V^2 , V^3 , and H^4 closed. Then if the pump P be set in action a portion of the oil in W^1 is sucked through the pipe I and forced through the inner nozzle D^1 of the mixing apparatus. This causes a circulation of a slower stream of the oil upward through the casing D^{3*} . Between the stream flowing in the apparatus from the lower part to upper part of the casing D^{3*} and the stream from the nozzle D^1 the required quantity of fuming sulfuric acid is run in from the vessel O through nozzle D^2 . The agitation through the apparatus can be continued as long as may be desired. The compressed air can be blown in to stir gently till the acid pitchy matter has balled itself together, and for the rest the procedure is identical with that already described. Another method of working with this arrangement of apparatus is as follows: In the agitator W^1 the oil can be subjected to a preliminary treatment with concentrated sulfuric acid in order to free it from water. For this purpose it is stirred with compressed air from the pipe M^1 . The acid is then run off through H^1 , whereupon the valve H^1 is closed and the valves V^1 and V^2 are opened and the suction and force pump P is put into action. Hereby the petroleum is forced through the mixing apparatus, where it is intimately mixed with the fuming sulfuric acid exactly in the manner hereinbefore described. The mixture passes on through the valve V^2 into the agitator W^2 . In W^2 the mixture can then be agitated with air forced through pipe M^2 until the pitchy matters ball together, when they are allowed to settle and finally to run off by opening valve H^2 .

If it is necessary to treat the oil with ordinary concentrated sulfuric acid in accordance with the second part of the invention,

the petroleum is worked over in an analogous way through the mixing apparatus from W^2 to W^1 , while the corresponding quantity of acid runs in from O . It is again mixed with air in W^1 and finally the pitchy matters run off. The treatment with water and alkali can either be effected in W^1 or in another agitator. In the meantime a new portion of oil can be freed from water in W^2 and further treated, as described.

If desired, a series of agitators can be fitted up side by side with the mixing apparatus between them; and in each one a particular operation can be effected, the working then being continuous.

To further illustrate the nature of my invention and the manner in which it can practically be carried into effect, I give the following examples:

Example I—Treatment of a cracked-up petroleum.—To a cracked-up Galizian petroleum specific gravity of about 0.820 add about one quarter per cent. of its weight of ordinary concentrated sulfuric acid (containing, say, about nine-six per cent. H_2SO_4) and stir in the usual way with air. This preliminary operation is intended to extract the water from the oil. Next force a portion of the petroleum through the inner nozzle D^1 of the apparatus, Fig. 1, while allowing one per cent. of the weight of petroleum of fuming sulfuric acid (containing about ten per cent. free anhydrid, SO_3) to run in through nozzle D^2 . When the admixture is complete, stir with air until the pitchy matters ball together. Allow these to settle and run off. Next treat with about one-half to one part, by weight, of ordinary concentrated sulfuric acid to one hundred parts of oil, mixing the acid in either through the apparatus or by stirring with air. Allow the pitchy matters to settle and then run off. The washing with water and alkali may be effected in the usual way. By "cracked petroleum" is meant petroleum whose heavy oils have been decomposed, the heavy oils as understood being those of a density equal to or denser than 25° Baumé.

Example II—Treatment of a petroleum distillate which has not been cracked up.—Free the oil from water exactly as described in example I. Then mix in one part, by weight, of fuming sulfuric acid (containing about twenty per cent. free anhydrid, SO_3) to every hundred parts of oil by means of the mixing apparatus. Subsequently stir with air and allow the pitchy matters to settle. Run these off and proceed to the washing with alkali and water in the usual way.

Example III—Treatment of a heavy oil.—Mix three parts, by weight, of fuming sulfuric acid (containing about five per cent. free anhydrid, SO_3) to every hundred parts of heavy oil previously free from water. This admixture may be effected with air in the ordinary well-known way. Subsequently stir more gently with air until the pitchy

matters ball together. Allow these to settle as far as possible and remove them. Then stir again with air and add about one part, by weight, of concentrated sulfuric acid per hundred parts of oil. Allow the pitchy matter to settle and proceed to the washing with water and alkali in the usual way.

Example IV—Treatment of benzene.—Stir and mix the dry benzene with the aid of the mixing apparatus with about half a part, by weight, of fuming sulfuric acid (containing about twenty per cent. free anhydrid, SO_3) to every hundred parts of benzene, putting the apparatus into action by pumping a portion of the benzene itself through the inner nozzle of the apparatus. When the mixture has settled, remove the pitchy matters and wash the benzene with water and alkali in the usual way.

The so-called "light unrefined photogene-oil" obtained from Thuringian coal-shale, and also ordinary benzene from coal-tar, can be refined in the manner described in the last example. In the former case about two parts, by weight, of fuming sulfuric acid (containing about twenty per cent. free anhydrid, SO_3) per hundred of oil are used; and in the case of the coal-tar benzin about four per cent. of its weight of fuming sulfuric acid containing from twenty to twenty-five per cent. free anhydrid (SO_3) may advantageously be applied.

Instead of air for the agitation of the unrefined oils other gases can be used—such as carbonic acid, nitrogen, or the natural gas which frequently occurs in petroleum districts. This is especially to be recommended in the case of oils which become oxidized on treatment with air.

It should be noted that the nozzles are not necessarily of circular form. A stream from a nozzle of circular cross-section has less surface exposure or less surface exposed to contact than one flowing from a nozzle with a slit opening. The cross-section of the nozzle is thus a matter which can be regulated according to judgment or circumstances.

While I have described novel apparatus which is especially adapted for working my invention and which I at present prefer to employ, it will of course be understood that my process claims are not limited to such or equivalent apparatus and that the invention

covered thereby may be worked by any suitable means.

This treatment could be applied to the oil as it comes from the well, but I prefer to apply such treatment to the distillate or distillates of such oil.

What I claim as new, and desire to secure by Letters Patent, is—

1. The process of refining petroleum and analogous oils which consists in injecting a stream of sulfuric acid between two streams (one of which is oil) moving at different velocities, substantially as described.

2. The process of refining petroleum and analogous oils which consists in injecting a stream of sulfuric acid between two streams (one of which is oil) moving at different velocities, said oil and acid being made to stream in parallel directions, substantially as described.

3. The process of refining petroleum and analogous oils which consists in injecting a stream of fuming sulfuric acid between two streams of oil moving at different velocities then treating the said oil with non-fuming sulfuric acid to remove acid-impurity combinations and then washing the oil, substantially as described.

4. A refining apparatus comprising a cylindrical casing provided with concentric inlet or injection nozzles and having a constricted portion above the nozzle-mouths and below the upper extremity of the casing; said casing having its upper portion provided with a lid and its lower portion provided with lateral inlets, substantially as described.

5. A refining apparatus comprising a cylindrical casing provided with concentric inlet or injection nozzles and having a constricted portion above the nozzle-mouths and below the upper extremity of the casing combined with a tank or vessel (one or more) made to communicate with the lower part of the casing, substantially as described.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

HERMANN WOLF.

Witnesses:

GUSTAV LICHTENBERGER.

ADOLPH REUTLINGER.