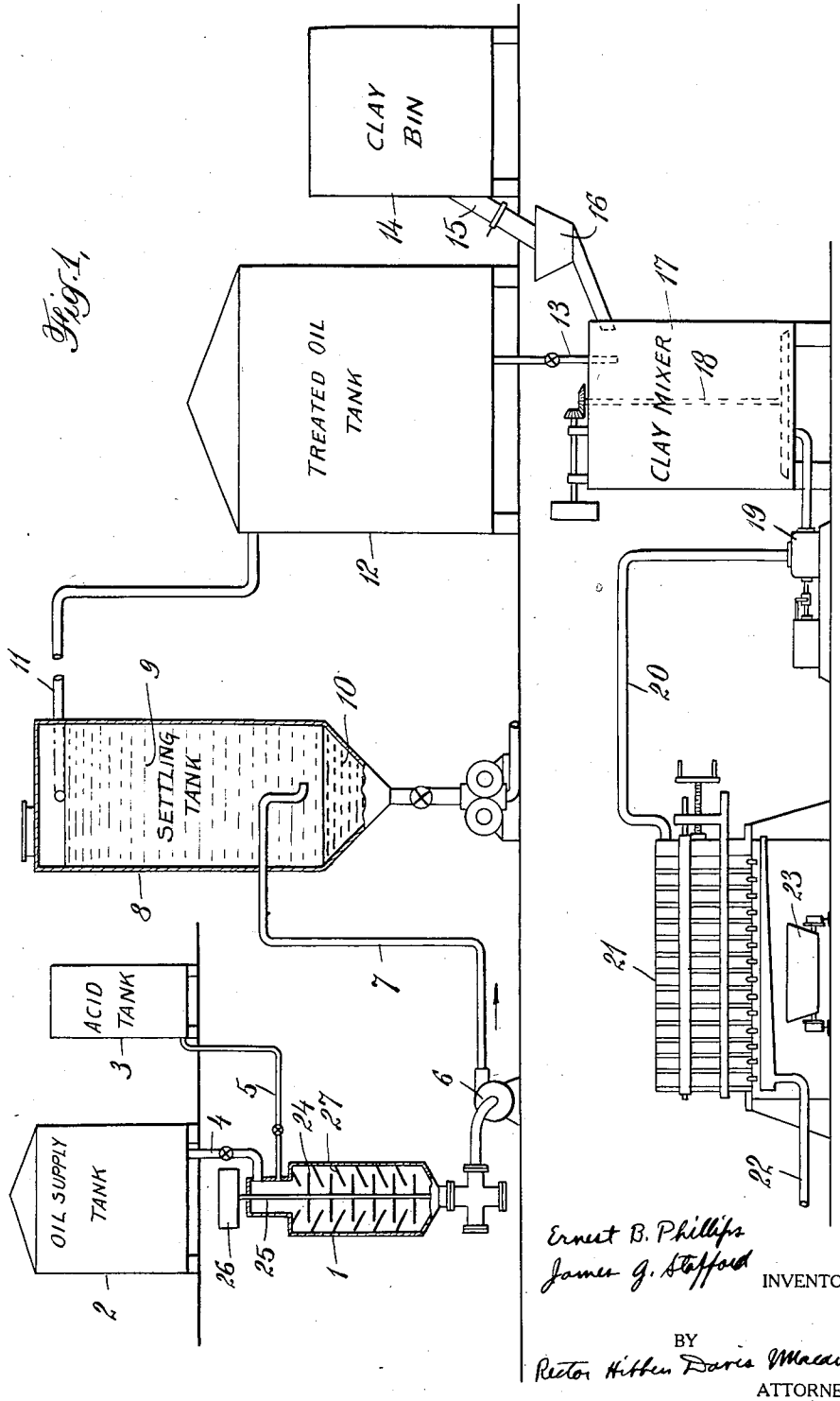
April 16, 1929. E. B. PHILLIPS ET AL 1,709,149

REFINING OF PETROLEUM

Filed Aug. 7, 1923 2 Sheets-Sheet 1

Fig. 1.



Ernest B. Phillips
James G. Stafford INVENTORS

BY
Rector Hibben Davis & Macauley
ATTORNEYS

April 16, 1929. E. B. PHILLIPS ET AL 1,709,149

REFINING OF PETROLEUM

Filed Aug. 7, 1923 2 Sheets-Sheet 2

Fig. 2,

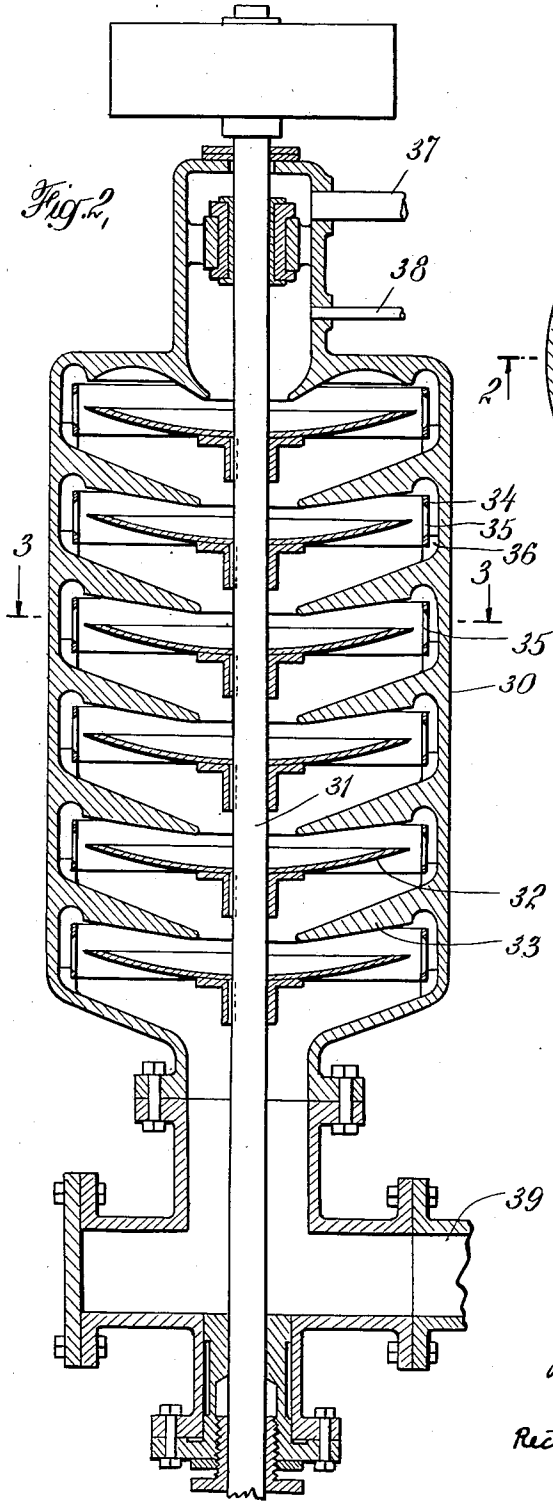


Fig. 3,

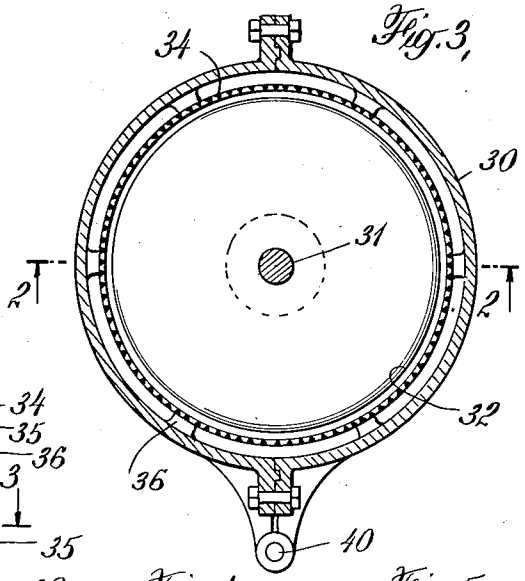


Fig. 4,

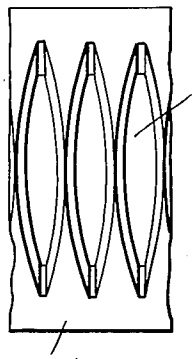


Fig. 5,

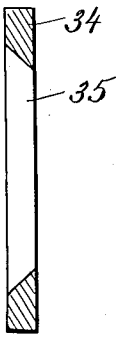
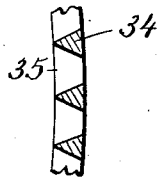


Fig. 6



Ernest B. Phillips
James G. Stafford
INVENTORS

BY Rector Hitten Davis & Macauley
ATTORNEYS

Patented Apr. 16, 1929. 1,709,149

UNITED STATES PATENT OFFICE.

ERNEST B. PHILLIPS, OF EAST CHICAGO, INDIANA, AND JAMES G. STAFFORD, OF CHICAGO, ILLINOIS, ASSIGNORS TO SINCLAIR REFINING COMPANY, OF CHICAGO, ILLINOIS, A CORPORATION OF MAINE.

REFINING OF PETROLEUM.

Application filed August 7, 1923. Serial No. 656,181.

This invention relates to an improved method and apparatus for refining hydrocarbon oils, such as natural and reduced crude oils and distillates therefrom. More particularly, the invention relates to improvements in the refining of hydrocarbon oils with sulphuric acid.

In the production of high grade products such as various types of lubricating oils, it has been the practice to select high quality crude oils as the material to be treated; and, as long as such high quality crude oils were available, grades could be selected for special purposes and high grade products uniformly made therefrom. However, with the tremendous increase in the demand for lubricants of various types coupled with the gradual exhaustion of superfine crude oils, the problem of obtaining high grade products from crude oils of lower quality becomes of increased importance.

Since the beginning of the petroleum industry, it has been the practice to refine petroleum oils with sulphuric acid by adding the acid to the raw products in lead lined tanks called agitators where violent agitation is produced by forcing large volumes of low pressure air through the oil and added acid. It has also been the common practice to treat the oil subsequently with alkaline solutions in an attempt to neutralize the excess acid and acid compound. Those portions of the raw product which unite with the sulphuric acid are converted into thick tar-like masses which under the conditions of air agitation are broken up into fine particles and distributed through the entire mass. When the acid treating step is complete, small quantities of water are added to the acid oil to "gather" the small particles of sludge and cause them to settle when the batch has come to rest. The oil is thereafter treated with the alkaline solution.

The treatment of the oil with sulphuric acid in the manner described, according to established practice, removes some, but not all, of the objectionable constituents of the raw material treated; but, in addition, such acid treatment at the same time causes certain injuries to the oil and introduces undesirable compounds into the oil which are difficult or impossible of removal by the subsequent alkaline treatment. The simultaneous action of acid and oxygen of the air upon the oil has an oxidizing effect which is made evident by the release of sulphur dioxide from the acid, and which results in secondary chemical reactions, the nature of which is somewhat obscure, which throw back undesirable compounds into the oil. The presence of these compounds in the acid-treated oil complicates the treating process and calls for additional steps to bring about their removal, and it is sometimes difficult or impossible to effect complete removal of them. After the acid treated oil is neutralized with alkaline solutions, trouble is often met with because of the formation of emulsions which can be overcome only by prolonged washing with water. The oxidizing treatment of the oil by the use of air agitation during the acid treatment not only injures the oil but frequently increases the difficulty of separating the acid sludge from the treated oil, and, even when so-called breaking water is used, a clean separation is often difficult or impossible; while the subsequent steps in the treating process, involving the use of alkaline solutions for neutralization, are seriously interfered with and the finished products still carry undesirable impurities. These difficulties and objections of the established sulphuric acid refining practice are particularly pronounced in the case of crude oils and residues which contain asphaltic constituents, such as the average mid-continent crudes or reduced crudes; and it is difficult or impossible to refine such crude oils in the manner indicated and obtain refined oils from which high grade lubricants can be produced by the usual refinery methods.

The present invention provides an improved method of refining hydrocarbon oils with sulphuric acid whereby the objections above referred to incident to the present refinery practice are overcome, and the production of high grade products is made possible; while the improved refining method of the present invention presents added advantages, hereinafter more fully set forth. The present invention also provides an improved apparatus for carrying out the new process.

The process of the present invention is carried out without the introduction of atmospheric air and with avoidance of oxidation resulting therefrom; and the oil is treated with sulphuric acid in a substantially continuous manner and with intimate contact of the oil and acid so that the sludge can be

readily separated from the treated oil. The treated oil, after the sulphuric acid treatment, is permitted to settle, and any remaining acid compounds are subsequently removed by a clay or fuller's earth treatment.

The method and apparatus of the present invention are of more or less general application for the treatment of various grades of raw and partially refined petroleum products, and including crude oils, both natural and reduced, as well as fractions and residuum produced therefrom. The invention is of particular value, however, in the refining of crude oils and residuum therefrom for the production of high grade lubricating oils, such as engine oils and cylinder stocks.

The invention will be further described in connection with the accompanying drawings illustrating the apparatus of the invention which is adapted for the practice of the process of the invention. The drawings are somewhat diagrammatic and conventional in character; and it will be understood that the invention is illustrated thereby and by the accompanying description, but is not limited thereto.

In the accompanying drawings Fig. 1 shows an arrangement of apparatus partly in section and partly in elevation.

Fig. 2 is an enlarged vertical sectional view showing a somewhat modified construction of the treater for treating the oil with acid taken on the line 2—2 of Fig. 3.

Fig. 3 is a horizontal sectional view taken on the line 3—3 of Fig. 2, and

Figs. 4, 5 and 6 are enlarged views showing the construction of the perforated ring member of Figs. 2 and 3.

Referring first to Fig. 1, a mechanical treater is shown at 1 which consists of a series of cells located one above another and with rotary baffles carried by a vertical shaft. The oil to be treated and the sulphuric acid to be used in the treatment are supplied from the storage or supply tanks 2 and 3 respectively through pipes 4 and 5 having suitable regulating valves therein. Leading from the bottom of the treater is an outlet for the oil and acid tar which are pumped by the pump 6 and carried through the pipe 7 to the settling tank 8, or to the first of a series of settling tanks. In such settling tank or tanks the acid tar separates from the oil and the oil overflows through the pipe 11 either to another settling tank or to a receiving tank 12 for the acid-treated oil while the acid sludge 10 collecting in the bottom of the settling tank is drawn off and pumped to an acid recovery plant.

From the tank 12 the acid-treated oil passes through the pipe 13 to the mixing apparatus 17 and clay or fuller's earth from the storage bin 14 is supplied through the chute 15 and hopper 16 in regulated amount. The treated oil is thoroughly agitated with the fuller's earth, and, when the treatment is complete, the oil and earth are pumped by the pump 19 through the line 20 to a pressure filter 21 from which the finished oil is discharged at 22. In the treater 1 a series of rotary baffles 24 are carried by the shaft 25 which is driven by a pulley or other suitable mechanical means 26. These rotary baffles are arranged at approximately the center of each cell between the side baffles 27. When the discs are rapidly rotated, the oil and acid introduced at the top of the treater flows down over the discs and is thrown by the discs outwardly against the walls of the apparatus. The separate streams of oil and acid flowing on the highest disc are thus caused to intermingle and are thrown by centrifugal force against the walls of the apparatus and are thoroughly mixed, this intermixture being promoted by the impact. The mingled oil and acid then flow down the walls of the upper cell and are collected by the conical baffle and delivered to the next lower disc, and this operation is repeated as the mingled oil and acid flow downwardly through the treating apparatus. The repetition of the intimate intermixture of the oil and acid during their passage downwardly through the successive cells and over the successive baffles brings about thorough treatment of the oil with the acid.

It will be evident that the size and construction of the treater 1 can be varied and a sufficient number of cells and baffles provided to insure thorough intermixture and treatment of the oil with the acid so that the oil and acid sludge will finally be delivered to the outlet line of the treater and carried to the sludge settling tank or tanks ready for settling of the acid sludge from the treated oil. In practice, a series of settling tanks may be used, for example, three in number, to insure proper settling of the acid sludge from the treated oil.

It is one advantage of the invention however that, because of the relatively mild handling of the oil and acid in the treater, and the absence of oxidation by atmospheric air, the acid-treated oil and acid sludge are easily separated, and clear settled oil readily obtained carrying only traces of impurities.

This acid-treated oil does not require a subsequent alkaline treatment, and it is a further advantage of the invention that such alkaline treatment can be eliminated.

For final purification of the acid-treated oil, a small amount of fuller's earth or equivalent material, in a finely divided state, for example, of 100 mesh or finer, is added to the oil and thoroughly mixed therewith. Thus in the apparatus illustrated, the acid-treated oil is thoroughly agitated with a small amount of fine fuller's earth in the mixer 17, and, when the earth treatment is complete, the combined oil and earth are withdrawn

and passed through a pressure filter to separate the earth and impurities and to give the finished oil.

In the treatment of the oil with acid, and also in the treatment of the acid-treated oil with fuller's earth, the oil can be heated (by means not shown) and held at the required temperature.

The pressure filter employed for removing the earth from the oil may be of any suitable type but is shown as a pressure filter of the leaf type. The press cake may be washed in the filter to free it from oil, for example, by washing out heavier oil with naphtha and by then removing the naphtha with steam, and the spent earth cake after such washing and steaming operation may be removed from the press into a dump car 23 and discarded or restored by subsequent treatment.

In Figs. 2 to 6 an improved form of treater 30 is shown of the same general type as the treater 1 of Fig. 1. The improved form of treater 30 of Fig. 2 has a central shaft 31 suitably mounted and supported therein and carrying a series of baffles 32. The outer shell of the treater carries side baffles 33 extending inwardly and dividing the treater into a series of cells similar to those of the treater of Fig. 1. Arranged within each cell is an annular ring 34 supported and spaced away from the sides of the cells by spacing and supporting members 36 and having a series of holes 35 extending therethrough of the shape and arrangement illustrated. The inlets for the oil and acid are indicated respectively at 37 and 38 and the outlet for the treated oil and acid at 39.

The casing illustrated is made up of two parts hinged together and with the two parts so constructed that the casing can be bolted together to form in effect a unitary casing.

It will be noted that the rotating baffles 32 are shaped somewhat in the shape of a saucer so as to retard the escape of the acid and oil and bring about a more thorough intermixture. The shape and construction of the cell walls and the arrangement of the baffle rings 34 are also such as to promote thorough intermixture of the oil and acid.

It will be understood that the apparatus will be made of or lined with material resistant to the action of the acid and that the shape and design and arrangement of the different parts of the apparatus can be varied. The action however is such that the acid and oil are subjected to a most intimate and thorough intermixture while protecting the oil from oxidizing conditions such as are present when air agitation is employed. As a result such acid compounds as are formed in the oil are in such condition that they are readily removed by the subsequent fine earth treatment and can therefore cause no injury in the finished oil.

The process will be further illustrated by the following specific example showing the treatment of reduced Burbank crude oil for the production therefrom of 650° F. fire test, steam refined, cylinder stock. The reduced crude treated had a gravity of 30.7, a flash point of 185° F., a fire test of 230° and a viscosity of 80 at 100° F.

This oil was heated to a temperature of 120° F. and was fed to the treater together with 66° Bé. sulphuric acid in the proportion of 13 lbs. of acid per barrel of oil. The oil and acid sludge mixture from the treater was pumped continuously to the first sludge settling tank, and the partially cleared oil rising to the top of this tank overflowed into a second settling tank, while liquid acid sludge settling at the bottom of the first settling tank was withdrawn at intervals and stored for recovery of its acid content. The first settler was held at a temperature of about 90° F. while the top of the second sludge settling tank was held at about 120° F. and the bottom at about 90° F. by suitable heating devices. The clear oil from the second settling tank overflowed into the storage tank for the treated oil.

Suitable batches of the acid treated oil were drawn into the earth mixer and finely divided raw fuller's earth of 100 mesh or finer was added in the proportion of 4% by weight of the oil. The batch was warmed to 175° F. and thoroughly agitated by the power operated stirrer for a period of about 30 minutes until the treatment was complete.

The batch was then transferred, with the stirrer still in motion to keep the earth in suspension, to a filter press by means of a pump in order to separate the suspended earth from the treated oil. The piping was so arranged that the first runnings from the filter, which were somewhat cloudy, could be returned to the main batch. When the stream from the filter press became clear it was cut into the storage tank for the treated oil.

At the end of the filtering operation, the press cake was washed with naphtha until free oil was removed and the washing added to the original filtrate. When the press cake was free of oil, steam was turned in to dry the earth mass and permit of easy discharge when the filter was opened. After dumping, the filter was ready for another cycle of operations. The spent earth from the filter may be restored for use if desired.

It will be evident that the size of the apparatus and the amount of oil treated can be varied, depending upon the amount of oil requiring treatment, etc. It will also be evident that a series of smaller treaters can be used in place of a single large treater.

In the process of the above example the oil was treated with a sludge loss of 7.4% and a yield of 92.6% obtained of an acid treated oil of 31.7 gravity. After the fuller's earth

treatment a yield of refined oil of 90.2% of the original stock was obtained in the form of the filtrate and an additional 1.9% from the washings with a loss of only 0.5% with the earth.

The untreated crude oil was of a character which could not be satisfactorily refined by the established refining methods, but the oil refined in the manner above described was a high grade product adapted for steam distillation for the production therefrom of steam refined lubricating oil. From the treated oil on distillation a yield of 74.2% of gas oil was obtained of 33.6 gravity, and a yield of 17.3% of steam refined cylinder stock of 21.9 gravity, 570° F. flash point, 650° F. fire point, a viscosity of 202 at 210° F., a pour test of 50, of a full steam refined green color, with a carbon residue of 3.76%, an ash residue of 0.03% and an insoluble content in 86° naphtha of 0.078%. The complete refining and distilling operation was carried out with a treating loss of 7.4%, a filter loss of 0.5% and a distillation loss of 0.6%.

We have treated in a similar manner raw crude oils varying in quality from average pipe line mid-continental grade to the usual Pennsylvania grade with equally good results. The net loss on treating varies somewhat with the quality of the oil, but the finished products are uniformly of high quality.

It will thus be seen that the present invention provides an improved method and apparatus for refining hydrocarbon oils which are of particular value in the refining of crudes or reduced crudes of middling grade, such as the average mid-continent crudes or reduced crudes, for the production therefrom of refined oils which are adapted for direct treatment by steam distillation for the recovery of high grade lubricating oils and other oils therefrom.

It will be evident that the invention presents many advantages. Among these advantages may be mentioned the following: The equipment required is compact and can be assembled in a relatively small space; the process is practically continuous and permits of large daily throughput; the regulation of the degree of treatment for a given oil is simple, and no long periods of settling and washing are required, while positive control of the treating operation is nevertheless assured; destruction of acid by oxidation with air and by release of sulphur dioxide, and formation of objectionable oxidation products, are avoided; no injurious secondary reaction products are formed in the oil and no neutralizing step with alkaline solutions is required; the treating losses are reduced to a minimum while the products from the oils treated are uniform in character and of high quality, and these oils can be produced at a less cost per barrel than by established methods; and the invention makes possible the production of oils of superior quality from raw materials which cannot be satisfactorily treated by established refinery methods, thus extending the field of oils from which high grade lubricants can be obtained.

In its broader aspects, the invention, as above stated, is of more or less general application; but we consider the invention to be of special value and application for the treatment of crude oils or reduced crudes which cannot be refined with sulphuric acid according to ordinary methods, but which can be easily and satisfactorily refined according to the present invention to give refined oils which can be subjected to steam distillation for the recovery of high grade lubricating oils therefrom.

We claim:

1. An apparatus for the treatment of oil with sulphuric acid comprising a vertical treater having a series of superimposed cells therein, a series of imperforate disks arranged horizontally within the separate cells and mounted on a vertically disposed rotating shaft, inwardly extending baffles between each of said disks, means for supplying streams of oil and acid to the upper end of the treater in regulated amounts, means to cause mixed streams of oil and acid to be repeatedly and successively distributed and thrown outwardly against the cell walls in a thin film and means for removing the treated oil and acid from the treater in a continuous manner.

2. An apparatus for the treatment of oil with sulphuric acid comprising a vertical treater having a series of superimposed cells therein, a series of imperforate disks arranged horizontally within the separate cells and mounted on a vertically disposed rotating shaft, inwardly extending baffles between each of said disks, means for supplying streams of oil and acid to the upper end of the treater in regulated amounts, means to cause mixed streams of oil and acid to be repeatedly and successively distributed and thrown outwardly against the cell walls in a thin film, means for removing the treated oil and acid from the treater in a continuous manner, means for separating the acid tar from the oil and means for subsequently subjecting the oil to treatment with a finely divided absorbent material.

3. An apparatus for the treatment of oil with sulphuric acid comprising a vertical treater having a series of superimposed cells therein, a series of imperforate disks arranged horizontally within the separate cells and mounted on a vertically disposed rotating shaft, inwardly extending baffles between each of said disks, means for supplying streams of oil and acid to the upper end of the treater in regulated amounts, means to cause mixed streams of oil and acid to be repeatedly and successively distributed and thrown out-

wardly against the cell walls in a thin film, means for excluding air from the treater and means for removing the treated oil and acid from the treater in a continuous manner.

4. The improvement in the refining of petroleum oils with sulphuric acid which comprises intermingling streams of the oil and the acid in regulated amounts, rapidly rotating a disk while supplying a stream of the oil and acid mixture to the upper surface thereof, whereby the oil and acid mixture is distributed over the upper surface of said disk and discharged in a thin film of uniform thickness around the outer entire edge thereof, subjecting the oil and acid mixture discharged from said disk to impact and subsequently separating the acid tar from the oil.

5. The improvement in the refining of petroleum oils with sulphuric acid which comprises intermingling streams of the oil and the acid in regulated amounts, rapidly rotating a disk while supplying a stream of the oil and acid mixture to the upper surface thereof, whereby the oil and acid mixture is distributed over the upper surface of said disk and discharged in a thin film of uniform thickness around the entire outer edge thereof, subjecting the oil and acid mixture discharged from said disk to impact, and subsequently treating the oil with a finely divided absorbent material.

6. The improvement in the refining of petroleum oils with sulphuric acid which comprises intermingling streams of the oil and the acid in regulated amounts, rapidly rotating a disk while supplying a stream of the oil and acid mixture to the upper surface thereof, whereby the oil and acid mixture is distributed over the upper surface of said disk and discharged in a thin film of uniform thickness around the entire outer edge thereof, subjecting the oil and acid mixture discharged from said disk to impact, and excluding air from contact with the oil and acid mixture throughout the foregoing treatment.

7. The improvement in the refining of petroleum oils with sulphuric acid which comprises intermingling streams of the oil and the acid in regulated amounts, rapidly rotating a disk while supplying a stream of the oil and acid mixture to the upper surface thereof, whereby the oil and acid mixture is distributed over the upper surface of said disk and discharged in a thin film of uniform thickness around the entire outer edge thereof, subjecting the oil and acid mixture discharged from said disk to impact, excluding air from contact with the oil and acid mixture throughout the foregoing treatment and subsequently treating the oil with a finely divided absorbent material.

8. The improvement in the refining of petroleum oils with sulphuric acid which comprises intermingling streams of the oil and the acid in regulated amounts, rapidly rotating a disk while supplying a stream of the oil and acid mixture to the upper surface thereof, whereby the oil and acid mixture is distributed over the upper surface of said disk and discharged in a thin film of uniform thickness around the entire outer edge thereof, subjecting the oil and acid mixture discharged from said disk to impact, subsequently permitting the acid-treated oil to settle, and treating the resulting oil with a finely divided absorbent material.

9. The improvement in the refining of petroleum oils with sulphuric acid which comprises intermingling streams of the oil and the acid in regulated amounts, rapidly rotating a series of disks while supplying a stream of the oil and acid mixture successively to the upper surfaces of each of said rotating disks, whereby the oil and acid mixture is distributed successively over the upper surfaces of each of said disks and discharged in thin films of uniform thickness around the entire outer edges thereof, subjecting the oil and acid mixture discharged from said disks to impact and subsequently separating the acid tar from the oil.

In testimony whereof we affix our signatures.

ERNEST B. PHILLIPS.
JAMES G. STAFFORD.