

Sept. 18, 1928.

1,684,489

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COUNTERFLOW TREATMENT OF PETROLEUM OILS

Filed Dec. 19, 1923

2 Sheets-Sheet 1

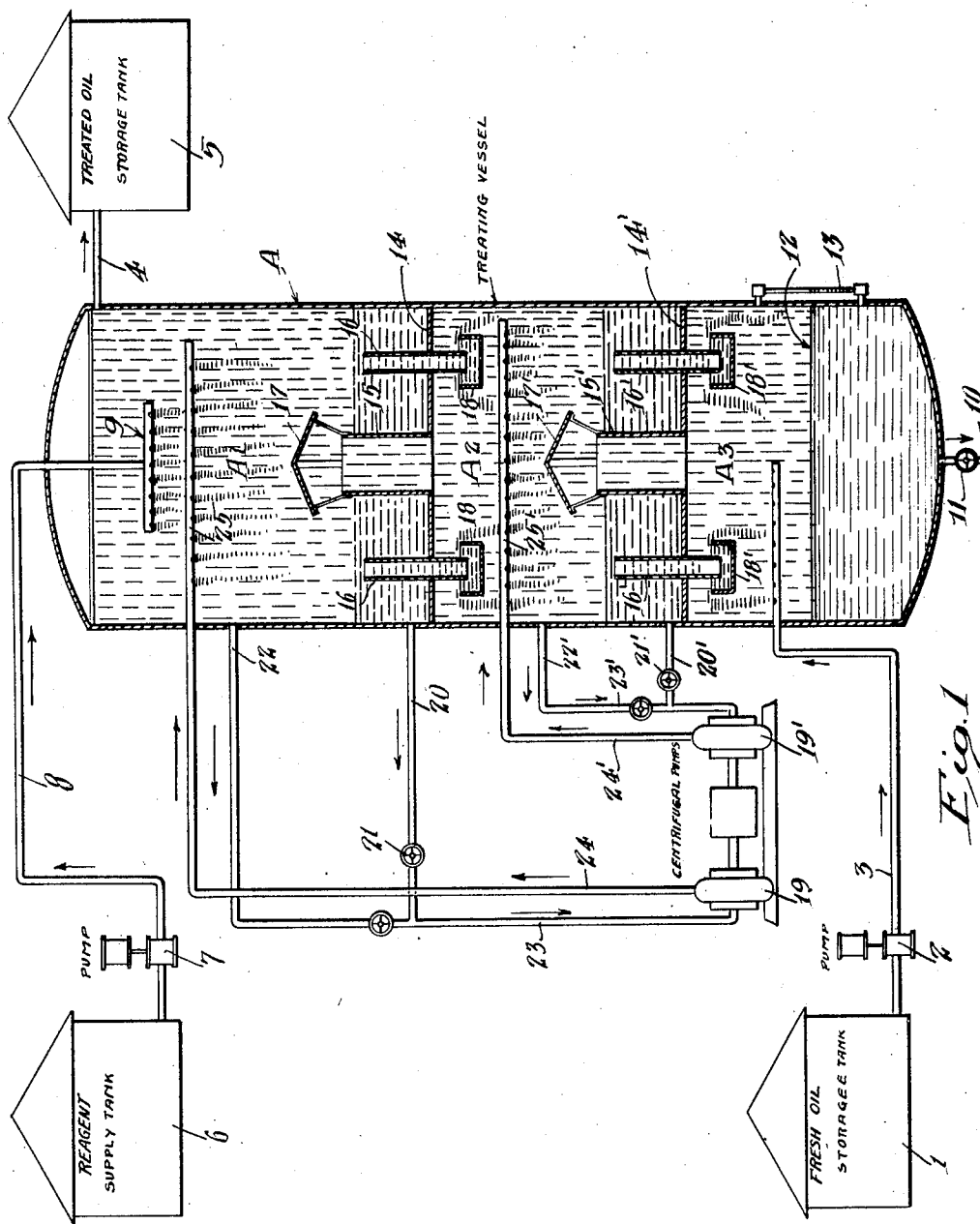


Fig. 1

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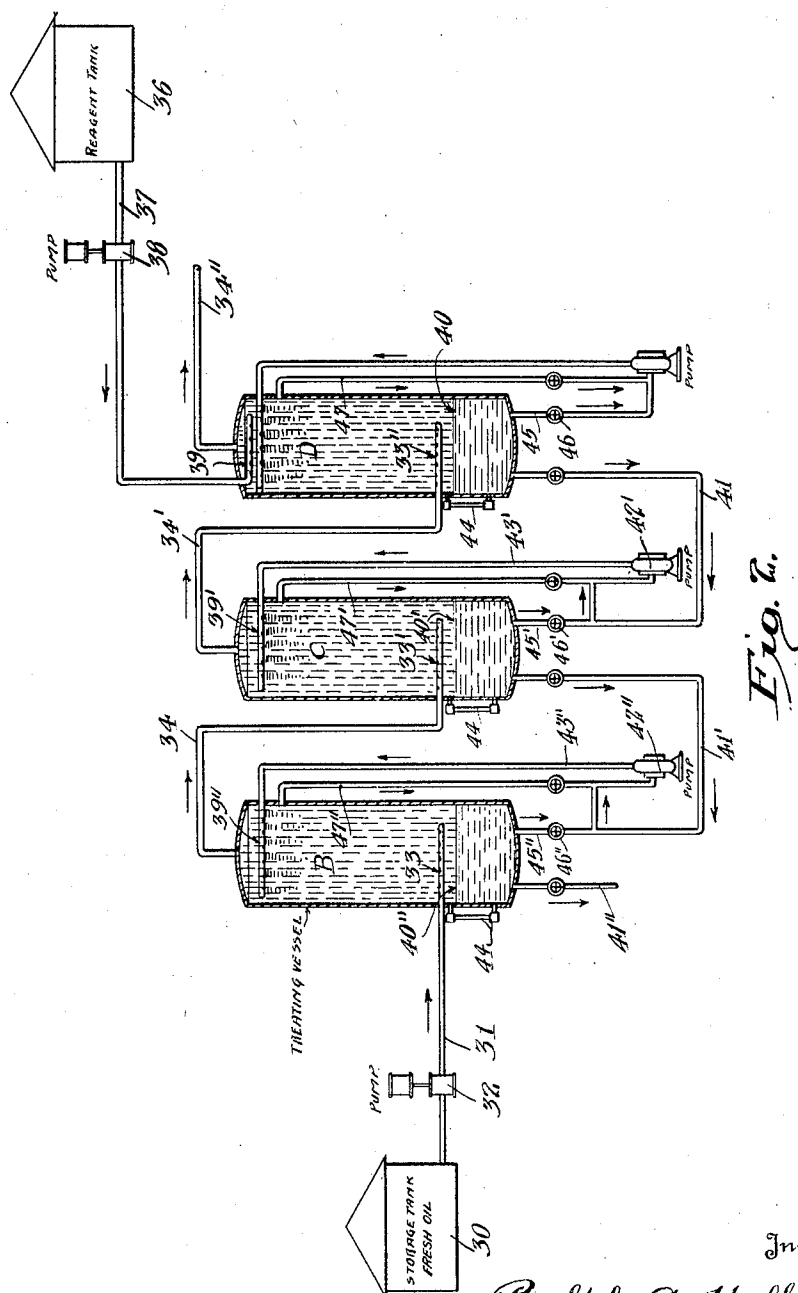


Fig. 2.

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UNITED STATES PATENT OFFICE.

RALPH A. HALLORAN, OF BERKELEY, CALIFORNIA, ASSIGNOR, BY MESNE ASSIGNMENTS, TO STANDARD OIL COMPANY OF CALIFORNIA, OF SAN FRANCISCO, CALIFORNIA, A CORPORATION OF DELAWARE.

COUNTERFLOW TREATMENT OF PETROLEUM OILS.

Application filed December 19, 1923. Serial No. 681,472.

This invention relates to a process of treating petroleum oils and refers particularly to the method of application of acid, alkali, water and washes of various sorts such as are employed during the manufacture of gasoline, lamp oils and other products from petroleum oils.

As heretofore practiced, the treatment of petroleum oils with different reagents has been attended with considerable inefficiency in utilizing that degree of strength in the reagents which is available for use in treating the oil. This is due to the fact that as commonly applied, the reagent acts first upon the most easily attacked ingredients of the oil, which ingredients are removed upon the first contact of the oil with the reagent, and as the oil becomes progressively harder to treat, the reagent in contact with the oil becomes correspondingly weaker. As a result, a condition is soon reached in which the reagent, while not entirely exhausted with reference to the fresh oil, has no more potential strength with reference to the oil with which it is in contact. If the oil, when this condition is reached, has not been acted upon to the desired degree, it must then be brought in contact with a fresh supply of the reagent.

Various methods have been employed to secure the desired efficiency in the utilization of the strength of the reagent applied to the oil. These have included improvements in mechanical mixing and air agitation devices for batch treating, as well as the use of nozzles and sprays for introducing the chemicals. Methods have also been devised for the continuous treatment of oil with chemicals. In these methods the chemical has been introduced continuously into a flowing stream of oil, or vice versa, so that both oil and chemical flow together through a treating vessel or through such mixing devices as small orifices, baffled pipes or mechanical mixers.

In both batch and continuous flow methods as heretofore practiced the ingredients of the oil most easily acted upon are removed upon the first contact of the oil with the fresh chemical. As the action continues, the oil becomes progressively harder to treat but at the same time must of necessity be acted upon by a chemical which has grown correspondingly weaker. As a result of this a condition is soon reached in which the chemical, while

not entirely exhausted with reference to fresher oil, has no more potential strength with reference to the oil with which it has been in contact. If the oil, when this condition is reached, has not been acted upon to the desired degree of completeness, it must then be brought in contact with a fresh supply of chemical which involves an additional labor cost together with complications which accompany additional applications of the chemical.

From the foregoing, it is evident that in the treatment of petroleum oils with reagents as heretofore practiced, all of the strength which is available in the chemical is not utilized and the spent chemical must contain considerable potential strength relative to the fresh oils or oils less completely treated, and considerably more of the reagents must be applied to the oil than should be necessary if the strength of the chemical could be properly utilized.

In my co-pending application, Serial No. 663,160, filed Sept. 17th, 1923, I have set forth a method whereby there is obtained a more complete utilization of the strength of the reagents employed in the treatment of petroleum oils than has heretofore been employed. The method as therein described provides that the reagents be applied to the oil in such a way that it will flow continuously in a direction opposite or counter to the direction of the flow of the oil receiving treatment, thereby bringing fresh or less exhausted reagent continuously in contact with the most fully treated oil, or, vice versa, bringing the progressively exhausting reagent in contact with the progressively fresher oil to be treated, all as more fully set forth in the application referred to above.

In the straight counterflow method as heretofore set forth in this co-pending application, the reagent is introduced at the top of a treating vessel in the form of a spray and descends as such to the bottom of the treater or to the accumulated mass of spent reagent and reaction products at the bottom of the treater. This descension of the reagent in finely divided form takes place against a rising current of oil. It will thus be noted that at any point in the treating vessel in which the counter current action is taking place, the ratio of partially exhausted reagent passing a given point to the oil undergoing treatment

passing that point is approximately the same as the ratio of new reagent to the new oil introduced into the treater. Practically the only thing that will make these two ratios differ from each other is the amount by which the volume of the oil is decreased by having been acted upon by the reagent and the amount by which the volume of the reagent is changed by the reaction products which are formed.

I have discovered that by increasing the amount of the partially spent reagent flowing counter to the oil at different points throughout the treating vessel so that at these points the ratio of reagent or partially spent reagent flowing counter to the oil undergoing treatment is increased by a material amount over and above the ratio of the new reagent to new oil being introduced into the counterflow treater, a marked improvement in the quality of oil produced by the straight counterflow method is effected and a better utilization of the potential strength residing in the reagent obtained.

I have also discovered a method of increasing the reaction between the reagent and oil in a counterflow treatment by withdrawing a part of the reacting mixture from the vessel and by mechanically commingling and agitating the same and then returning the mixture to the vessel, and by such commingling of the reagent and oil the quality of the oil produced is improved while still effecting a counterflow treatment.

My invention will be better understood by reference to the attached drawings which are given for illustrative purposes only, it being understood that the increasing of the concentration of the reagent within the oil undergoing counterflow treatment to such an extent that the ratio of the reagent flowing counter to the oil being acted upon within the treater is materially increased over and above the ratio of reagent to oil being introduced into the treater is not limited to the particular manner of accomplishing as herein set forth.

In the drawings, Figure 1 represents a single counterflow treater in which there is carried out a two-step phase of my process of increasing the percentage of reacting reagent within the treater to a point in excess of the percentage of new reagent being added to the oil.

Figure 2 represents a modification showing how the different steps can be carried out using individual counterflow treaters for each step. In addition, Figure 2 shows a three-step phase of my process.

Referring to Figure 1 of the drawings A represents a vertical treating vessel. 1 represents an oil storage tank from which the oil to be treated is forced by pump 2 through line 3 into vessel A, at a point near the lower end thereof. Because of this oil being of a lighter weight than the reagents (such as acid, al-

kali, water, etc.,) used for treating the same, it rises through the vessel A in a direction opposite or counter to the descending reagent which is conveyed by means of the pump 7 from a supply vessel 6 through pipe 8 and spray or spreading device 9 into the top of the treating vessel A. The oil which passes upward through the counterflow treating vessel A, passes out through pipe 4 into a storage vessel 5.

12 indicates the level of the sludge and spent reagents, which results from the treatment. This sludge and spent reagent is conveyed from the treater into pipe 10 and discharged into the sewer or other suitable place for disposal. The level 12 of this sludged material is controlled by the valve 11, located in the draw-off pipe 10.

13 represents a gauge for determining the location of the sludge level 12.

14 and 14' represent partitions in the treating vessel A, dividing it into compartments A₁, A₂ and A₃. The sludge formed in compartment A₁, together with the spent reagent, will accumulate on the bottom 14, of compartment A₁. Likewise there will be an accumulation of sludge and spent reagent on the bottom 14' of compartment A₂. Through the bottom or partition 14 there extend down-pipes 16. When the sludge accumulation on the partition or bottom 14 becomes sufficient to cause the sludge level to rise to the top of these down-pipes 16, it will overflow into these down-pipes and descend through into compartment A₂. Deflectors 18 are arranged underneath these down-pipes, in order to scatter or break up into small particles this descending sludge.

15 represents a pipe forming a passage-way for the rising oil to flow from compartment A₂ into A₁. This rising oil is scattered and broken up into small particles by means of the deflector 17. Likewise in the bottom or partition 14', there are similar down-pipes 16' and a passage-way 15'. Deflectors 18' are located below pipes 16' and a deflector 17' is located above passageway 15'.

19 and 19' represent centrifugal pumps which take suctions through pipes 22 and 22' on compartments A₁ and A₂, respectively from points near the upper ends thereof.

20 and 20' represent pipes which lead from compartments A₁ and A₂, respectively, at points near the bottom of these compartments and join the suction lines 22 and 22' respectively to form suction lines 23 and 23' for the centrifugal pumps 19 and 19' respectively. The points from which the pipe 20 and 20' lead from compartments A₁ and A₂ are located below the sludge levels which are formed in these compartments so that a portion of the accumulated sludge and spent reagent may be drawn through suction lines 20 and 20' respectively, and joined with the liquids which are drawn through suction

lines 22 and 22' respectively. Valves 21 and 21', located in the lines 20 and 20', respectively, provide means for controlling the quantities of sludge which are drawn into the pumps 19 and 19', respectively. The mixture of sludge from the bottom of each compartment A₁ and A₂ and the liquid drawn from the upper portions of these same compartments is discharged by the pumps 19 and 19' through the discharge lines 24 and 24' and through the spray nozzles 25 and 25', respectively, into the upper portions of compartments A₁ and A₂, respectively.

It will thus be seen that by drawing a part of the accumulation of partially spent reagent which forms in the bottom of compartments A₁ and A₂ into the suction lines of the centrifugal pumps and causing this partially spent reagent to join with the mixture of oil and fresher reagent from the tops of these compartments there is an addition of reacting reagent to the mixture of oil and reagent and that the percentage of reacting reagent in the oil is thereby materially increased. The amount by which this percentage may be increased is controlled by a regulation of the valves 21 and 21' located in the sludge suction lines. A material increase in the contact of the reacting reagent with the oil is thus obtained, because there is a much greater proportion of reacting chemical to make contact with a given quantity of oil. There is also the added advantage of securing a more intimate contact between the oil and the reagent because of the agitation which takes place in the centrifugal pumps. By discharging the mixture with its increased content of reacting reagent from the discharge spray lines located in the tops of the respective compartments, it is also seen that in those portions of the vessel in which the oil and reagent are contacting during their counterflow movements, there is an increased percentage of reacting reagent, or in other words, the ratio of reagent flowing counter to the oil where the treating or reaction is taking place is raised materially above the ratio of entering reagent to entering oil.

It will be noted that if the valve 21 in sludge suction line 20 is entirely closed so that all of the liquid fed to the pump 19 passes through the one line 22, the mixture then discharged through line 25 would have the same ratio of reagent to oil as in the intake line 22 or as elsewhere in the compartment. This ratio would be approximately equal to the ratio of entering reagent to entering oil and there would be only the addition to a straight counterflow treatment of the feature of mechanical mixing. The feature of mechanical mixing in such a process is a valuable feature of this invention which I desire to cover both with and without the increase of the ratio of reagent to reacting oil.

To illustrate more clearly how my process

effects an increase in the percentage of reacting reagent in the mixture, it will be seen that with the valve 21 and sludge suction line 20, I am able to introduce controlled quantities of added reacting reagent to the oil-reagent mixture undergoing reaction in the vessel and to thereby produce a ratio of reacting reagent, flowing counter, to the oil undergoing treatment, which ratio is in excess of the ratio of entering reagent to entering oil. Furthermore, I am able to control this increase in the percentage of reacting reagent by introducing the accumulated sludge and partially spent reagent into the suction line of the circulating pump in controlled quantities. When this increase in the ratio of reagent to oil is obtained, a marked improvement in the quality of treated oil over that obtained by the simple or straight counterflow process is effected.

Moreover in addition to the benefit obtained in the treatment within the vessel A the commingling of the mixtures drawn in the lines 22 and 22' with the reagent drawn in the lines 20 and 20' respectively, permits such mixtures during their passage through lines 23 and 23', pumps 19 and 19' and lines 24 and 24' to be thoroughly treated by the increase of the ratio of reagent to oil therein above the ratio of entering reagent to entering oil.

It will be apparent that the treating vessel may be divided into any desired number of compartments and the number of such circulating phases as described above increased to any desired number. It will also be apparent that the reagent need not be introduced into the top of the treater, as shown in the drawing. It may, for example, be introduced at a point in either the suction or discharge lines of the circulating pump of the first or upper compartment.

By arranging a number of such treating vessels in series it will be apparent that a treating plant can be arranged that will provide for the continuous treatment of an oil with a number of different reagents, such for example as a preliminary lye or alkali treatment, an acid treatment, a neutralizing step, and the necessary water washings. My process is not limited therefore to the action of a single reagent.

In the modified apparatus shown in Figure 2 in which the different phases of my process described in connection with Figure 1 may be carried out using individual vessels for each phase, B, C and D represent separate treating vessels arranged in a series for effecting the counter current treatment. When employing the apparatus in Figure 2 the oil to be treated is drawn from an oil storage tank 30 through a line 31 by a pump 32 and enters the vessel B at a point near the lower end thereof, preferably being discharged from a distributor or spraying device 33. The oil rises

in the vessel B and is drawn off at or near the upper end by a line 34 and introduced into the vessel C likewise at a point near the lower end thereof through a distributor or spraying device 33'. The oil flows upwardly through the treater C and is drawn off from the upper end through a line 34' and introduced into the treater D through the spraying device 33'' hence flowing upwardly through the treater and out through the final discharge line 34''. The treating reagent is drawn from the tank 36 and forced through a line 37 by a pump 38 into the upper end of the treating vessel D being discharged into the vessel from a spraying or distributing device 39 into the uprising oil therein. The reagent fed into the treater D passes down through the uprising oil and accumulates at the lower end of the vessel where it is maintained at a substantially fixed level 40. From the lower end of the treater the reagent is drawn through a line 41 by means of a pump 42' and forced through the line 43' into the upper end of the vessel C entering through a spray or distributing device 39'. The reagent likewise passes through the vessel C to the lower end where it is maintained at a level such as indicated by 40' and is continuously withdrawn through the line 41' by the pump 42'' and forced through the line 43'' into the upper end of the vessel B entering through the spray device 39''. Similarly the reagent passing into the vessel B descends against the uprising oil to the bottom of the vessel being maintained at a suitable level 40'' and continuously withdrawn through the line 41''. 44 indicates a number of level gauges, one of which is supplied to each vessel for indicating the sludge level maintained therein.

The lower ends of the treating vessels B, C and D are respectively provided with lines 45'', 45' and 45 controlled by valves 46'', 46' and 46 respectively by means of which part of the reagent collecting in the bottom thereof may be drawn by the pumps, such as 42'', 42' or 42 respectively, and forced upwardly through the lines 43'', 43' or 43 respectively, and discharged into the upper end of the respective treaters B, C and D so as to increase the ratio of reacting reagent to oil maintained in the respective treaters.

The lines 45' and 45'' may introduce the reagent back into the treaters through the same lines and pumps as the reagent first entering the treaters or separate pumps and lines may be supplied for such purposes.

47, 47' and 47'' indicate lines connected to the upper ends of the vessels D, C, and B respectively, by means of which part of the mixture of reagent and oil present in the respective vessels may be drawn from the vessels and commingled preferably with the reagent to be recirculated, and as in the treaters B and C, the mixture may further be com-

mingled with the reagent as it first enters the said vessels.

It is thus seen that by the apparatus described in Fig. 2 a three step or phase counter flow process embodying this invention may be practiced.

While the embodiments of the process herein described are well suited for the purposes of this invention, it is not intended to limit the invention to the details of the processes herein set forth for the purpose of illustrating the preferred examples of the invention, but various modifications may be made without departing from the spirit of the invention.

This invention is of the scope set forth in the appended claims.

I claim:

1. A process of treating petroleum oil with a reagent of substantially greater density than the oil and essentially immiscible therewith which includes flowing fresh oil continuously into a treating vessel and continuously flowing treated oil out of the vessel, simultaneously causing fresh reagent to flow continuously into the same treating vessel and the spent reagent and resulting sludge to flow simultaneously out of the vessel, causing reagent within the vessel to flow in a direction opposite or counter to that of the flowing oil, accumulating within a portion of the treater partially spent reagent, and circulating to and from a region in which the flow of chemical and oil is counter current a portion of this accumulation of partially spent reagent, together with such a portion of the oil being acted upon that the ratio of reacting chemical to oil being acted upon in a portion of the treating apparatus is in excess of the ratio of entering chemical to entering oil.

2. A process of treating petroleum oil with a reagent of substantially greater density than the oil and essentially immiscible therewith which includes contacting a progressively exhausting reagent with a progressively fresher or less-treated oil, simultaneously contacting the same oil as it becomes progressively more treated with a progressively stronger reagent, the reagent flowing in a direction opposed to the flow of oil, simultaneously accumulating a portion of the resulting partially spent reagent, and contacting such a quantity of this accumulated partially spent reagent with a mixture of progressively exhausting reagent and progressively more treated oil than the ratio of the quantity of reacting reagent flowing through a part of the vessel to quantity of flow of the oil in that part of the vessel becomes in excess of the ratio of the quantity of new reagent to new oil.

3. A process of treating petroleum oil with a reagent of substantially greater density than the oil and essentially immiscible therewith which includes flowing fresh oil con-

tinuously into a treating vessel and continuously flowing treated oil out of the vessel, simultaneously causing fresh reagent to flow continuously into the same treating vessel and the spent reagent and resulting sludge to flow simultaneously out of the vessel, causing reagent within the vessel to flow in a direction opposite or counter to that of the flowing oil, and simultaneously maintaining such a percentage of reacting reagent flowing counter to the oil that the ratio of the current of reacting reagent to the current of oil being acted upon, is in excess of the ratio of entering reagent to entering oil.

4. A process of treating petroleum oil with a reagent of substantially greater density than the oil and essentially immiscible therewith which includes passing fresh oil into a treating vessel and continuously passing treated oil out of the vessel, passing fresh reagent into the vessel and continuously passing the spent reagent out of the vessel in such manner that at least a part of the reagent passes counter to the oil, repassing a part of the reagent through a part of the vessel countercurrent to the flow of oil therein, and forming a mixture of reagent and oil while flowing in opposite directions in the treating apparatus in which mixture the ratio of reagent to oil is in excess of the ratio between the fresh entering reagent and entering oil.

5. A process of treating petroleum oil with a reagent of substantially greater density than the oil and essentially immiscible therewith which includes continuously passing fresh oil into a treating vessel and continuously passing treated oil out of the treating vessel, continuously passing fresh reagent into the vessel and continuously passing spent reagent out of the vessel so as to flow counter to the oil, withdrawing from the vessel a mixture of reagent and oil in which mixture the ratio of reagent to oil is in excess of the ratio of entering reagent to entering oil, and commingling and returning the mixture to the vessel.

6. A process of treating petroleum oil with a reagent non-miscible therewith, which includes bringing the oil and reagent into contact with each other in a treating path in which the oil enters the end of the path ad-

jacent the point at which the reagent is withdrawn from the path and in which the reagent enters the path adjacent the point the oil is withdrawn therefrom, withdrawing from the path a mixture of the oil and reagent and commingling the same and returning the same to the path, separating at least part of the reagent from the oil in one portion of the path, and recirculating part of said reagent again through a portion of the path to thereby enrich the proportion of reagent to oil passing through such portion of the path.

7. A process of treating petroleum oil with a reagent non-miscible therewith, which comprises continuously bringing streams of oil and reagent into contact with each other in a treating path in which the oil enters the path adjacent the point at which the reagent is discharged from the path and in which the reagent enters the path at a point adjacent where the oil is discharged from the path, removing admixtures of oil and reagent at a plurality of points in the treating path, commingling said mixtures, and returning the same to the path, and separating part of the reagent from the mixtures in the path and recirculating said separated reagent through a portion of the path so that the ratio of reagent to oil passing through that portion of the path is increased.

8. A continuous process of treating petroleum oils and with a liquid reagent substantially immiscible therewith comprising continuously supplying fresh oil into a treating vessel and continuously removing treated oil from such treating vessel, simultaneously continuously supplying fresh reagents to the treating vessel so as to cause the reagents to flow in a direction opposed to the flow of oil being treated, accumulating partially spent reagent within a portion of said treater and circulating said accumulated partially spent reagent countercurrent to the oil being treated so as to maintain a larger ratio of reagent to oil within said treater than the ratio of fresh reagent and oil supplied to said treater and removing spent reagent.

Signed at Richmond, Calif., this 11th day of December, 1923.

RALPH A. HALLORAN.