

April 3, 1934.

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1,953,618

ABSORPTION OF OLEFINES

Filed July 20, 1931

2 Sheets-Sheet 1

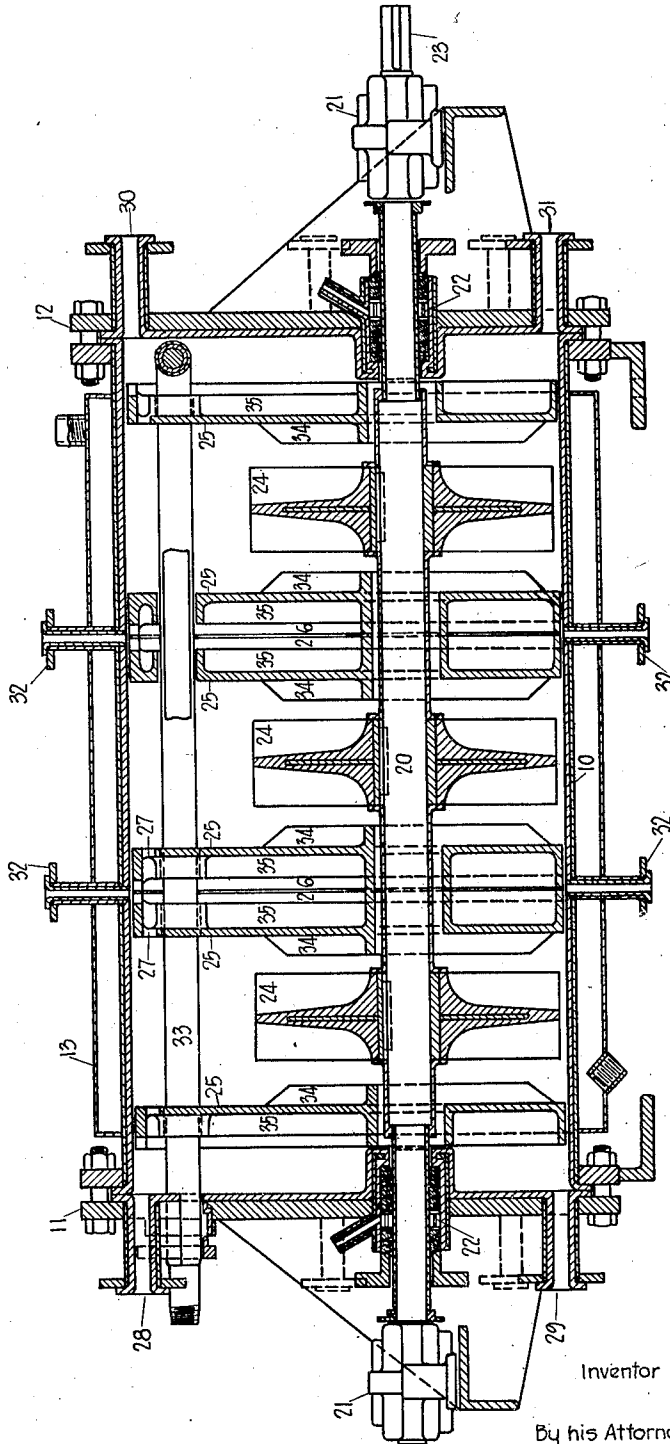


FIG. 1

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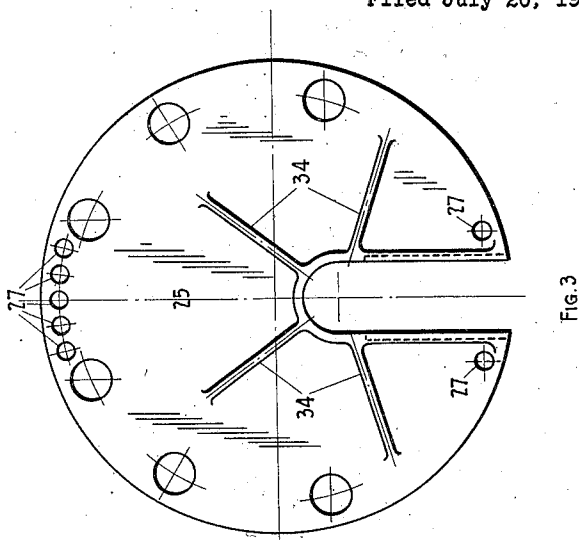


Fig. 3

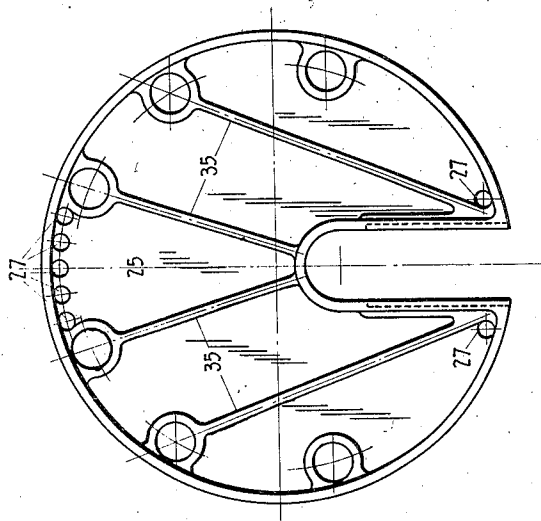


Fig. 2

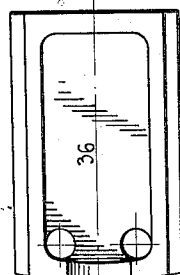
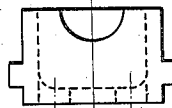


Fig. 4



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## UNITED STATES PATENT OFFICE

1,953,618

## ABSORPTION OF OLEFINES

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Application July 20, 1931, Serial No. 551,970

15 Claims. (Cl. 260—99.12)

This invention relates to a novel apparatus and process for contacting immiscible liquids with each other for the purpose of extraction, chemical treatment or the like, and more particularly to an apparatus and/or process wherein it is desired to carry out such contact in counter-current relationship of the two liquids.

The preferred process comprises passing two substantially immiscible liquids in counter-current flow to each other through a plurality of stages arranged in contiguous relationship and communicating with each at a plurality of points, each alternate stage containing an agitating means, the end stages being characterized as quiescent or separating zones and each end stage containing an inlet and outlet for the liquids undergoing treatment. The emulsified liquids in the agitating zones are maintained in a hydrostatic balance with the stratified liquids in the adjacent separating zones.

The foregoing and other objects and advantages of the invention, however, will be so clearly apparent to those skilled in the industry, as incidental to the following disclosure, that it would serve no useful purpose to further enlarge upon the same initially, and with these prefacing remarks, therefore, reference will now be had to the accompanying drawings, generally illustrating at least one practical embodiment of a novel systematic combination of means for carrying forth the steps of the method involved, although not essentially the only apparatus for doing so, in which drawings

Fig. 1 is a sectional side elevation of the apparatus carried out according to this invention;

Fig. 2 is a front elevation of a diaphragm;

Fig. 3 is a rear elevation of a diaphragm and

Fig. 4 is a plan view of a diaphragm closing piece.

In the drawings, wherein like characters of reference designate corresponding parts throughout the several views: 10 is a cylindrical shell provided with removable covers 11 and 12 and with an outer jacket 13 which may be utilized for heating or cooling the liquids in the mixer, should this be necessary. 20 is a shaft running parallel to the center line of shell 10 but preferably eccentrically located therein and supported in bearings 21. Stuffing glands 22 prevent leakage of liquids along the shaft when in motion, and specially formed end or ends of the shaft as shown at 23 permit connection to a prime mover by means of pulleys or couplings or the like. The shaft carries within the space enclosed by vessel 10, suitably spaced rotors 24 of any

desired number which when revolving, agitate the liquid contained in the mixing device, causing intermingling of otherwise not miscible liquids in more or less fine emulsions. Diaphragms 25 are so spaced that one pair of them form a substantially enclosed space 26 in which the agitation of rotors 24 is not felt and is of such size that the emulsions formed in the mixing compartments may separate due to differences in specific gravity of the liquids in question.

Such diaphragms may be also placed between each end rotor and end plates 11 and 12 of the mixing vessel, or they may be omitted and external separating vessels substituted for this purpose.

The diaphragms 25 are closed on shaft 20 by means of diaphragm closing piece 36 which permits rotation of the shaft without substantial leakage of fluids between compartments.

The agitating and separating stages are in communication through openings 27 suitably placed near the upper and lower peripheries of the diaphragms and of such a size that they permit liquid to circulate between the two stages without causing the turbulence of the mixing zones to be communicated to the separating zones. Vanes 34 tend to increase the turbulence and eddy flow in the agitating compartments whereas vanes 35 tend to straighten out eddy flow in the separating compartments thereby expediting stratification of the immiscible fluids. Openings 28, 29, 30 and 31 are provided for feeding into and discharging from the vessel 10, the materials to be inter-acted, while openings 32 may be provided for sampling the liquids at various steps of the process. Coil 33 may be provided for additional internal cooling, either by water or by other refrigerating media or may be utilized for heating purposes, if so desired, by the passage therethrough of hot water, steam or other heating media.

The operation of the device may possibly be best understood by first considering the rotors at rest and supposing that two immiscible liquids of different specific gravities, e. g., sulfuric acid and hydrocarbon oil have been placed into the apparatus so that practically the entire space within the shell 10 is filled with liquid. The two liquids will naturally rest in the device in such a manner that the heavier one occupies a lower layer, the lighter one resting on top as, for example, shown by the dividing line drawn in Fig. 1.

If now the rotors are set in motion, the two liquids in the mixing compartments will be

emulsified, but no substantial disturbance of the separated liquids occurs in the separating compartments because the total hydraulic head acting on openings 27 from the mixing compartment is still the same as that from the neighboring separating compartment. If we now remove some of the heavy liquid through opening 31, the deficiency will be made up by additional liquid flowing in through the openings of diaphragm 25. However, this incoming liquid contains not only sulfuric acid, but also admixed hydrocarbon, so that after separation of the two, the level of sulfuric acid in this compartment will be lower than that corresponding to the hydraulic head necessary to maintain equilibrium. Consequently, some additional liquid will flow into this separating compartment through the lower openings of the diaphragm 25 and some hydrocarbon through the upper openings of the diaphragm 25 back into the neighboring mixing compartment, until by separation of the incoming emulsion, sufficient acid has been accumulated to again establish equilibrium. Similarly, if the equilibrium were disturbed by feeding some additional acid into the opening 29, this acid will again disturb the hydraulic equilibrium and will force more acid through the lower openings of the neighboring diaphragm and so on through the entire device until equilibrium has again been reached.

By the same way, additional hydrocarbon fed into opening 30 would again be gradually distributed through the entire system, meanwhile being successively agitated with acid by the rotors in the mixing chambers.

If hydrocarbon is fed continuously into opening 30 and is being continuously removed at the same rate through opening 28, at the same time acid is being fed into nozzle 29 and being removed at the same rate through nozzle 31, it is easily understood that while the dividing levels in the separating compartments remain substantially unchanged, the acid and hydrocarbon come into thorough contact with each other in counter-current, fresh acid always being contacted with nearly fully treated hydrocarbon and untreated hydrocarbon with nearly fully spent acid.

The relative time of contact may be varied independent of the throughput. Assume the volumetric capacity of the shell to be 200 gallons and that it contains 100 gallons of each liquid, the hourly feed also being 100 gallons of each. The average contact time of each of the liquids will then be one hour. If the contents of the shell are changed to 50 gallons of the light liquid and 150 gallons of the heavy liquid, the throughput being kept at 100 gallons per hour for each of the liquids, then the average contact time for the light liquid will be reduced to one-half hour and that for the heavy liquid increased to one and one-half hours; the ratio of the contact times of the two liquids thereby decreasing from 1 to  $\frac{1}{3}$ . In similar manner, the relative time of contact of the light or heavy liquid may be either increased or decreased, depending on the character of the substantially immiscible liquids and the economic conditions of operation.

Under certain circumstances, it may be desirable to effect the contact of the two substantially immiscible fluids by means of parallel flow, in which case the lighter fluid is introduced at 30 and removed at the same rate through 28, while the heavier fluid is fed in at 31 and removed at the same rate through 29.

The number of agitating and settling chambers employed is dependent on the character of the liquids undergoing treatment and the nature of the process. For example, in parallel flow, an agitating chamber in communication with two settling chambers may suffice whereas in counter-current flow a plurality of agitating chambers is desirable, the efficiency of the process increasing with the number of agitating compartments.

By way of example only, reference will be had to the treatment of a mineral oil fraction consisting essentially of hydrocarbons containing four carbon atoms to the molecule with sulfuric acid of such strength, that the tertiary-base olefines contained therein, such as isobutylene, are selectively absorbed by the sulfuric acid and removed therewith, although it is to be understood that the process and apparatus is applicable to the treatment of any mineral oil fraction containing hydrocarbons of any number of carbon atoms to the molecule with an acid which may comprise  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HCl}$ , etc. Pentane-pentene and hexane-hexene fractions are very suitable for treatment by my process for the selective absorption and removal of tertiary-base olefines (olefines capable of yielding tertiary alcohols upon hydrolysis).

A butane-butene fraction containing approximately 15 to 20% by wt. of tertiary or gamma butylene is introduced at 30 while an equivalent amount of 65 to 70%  $\text{H}_2\text{SO}_4$  is introduced at 29. To insure the complete absorption and removal of the gamma butylene, about a 10% excess of 65 to 70%  $\text{H}_2\text{SO}_4$  is introduced at 29 (the amount of  $\text{H}_2\text{SO}_4$  to be added being calculated on the amount of isobutylene to be absorbed). The vessel 10 in the meantime has been filled with 65 to 70%  $\text{H}_2\text{SO}_4$  and the butane-butene fraction to be treated, the exact proportion of the contents of the vessel being dependent on the desired relative time of contact. The liquids flow in counter-current fashion, the efflux at 28 comprising the butane-butene fraction from which the isobutylene has been substantially removed while the efflux at 31 comprises  $\text{H}_2\text{SO}_4$  relatively saturated with isobutylene. The temperature is maintained between about 80° to 90° F. to avoid substantial polymerization of the butene-1 and butene-2. The pressure in the vessel is approximately the vapor pressure of the butane-butene fraction at the operating temperature.

The process and/or apparatus assure ease of control, simplicity and flexibility of operation and maximum yield in the optimum minimum time of contact.

It will be obvious that various substitutions in the materials treated and in the liquids used, as well as modifications in the order and manner of execution may be made in the practical application of the invention, but such substitutions and modifications are to be considered as comprehended by the above disclosure and included within the purview of the following claims.

I claim as my invention:

1. A process for the treatment of immiscible fluids comprising: flowing a tertiary-base olefine-containing fluid and an acid in counter-current through a series of alternate agitating and settling zones only the contiguous zones of which are in communication with each other, the ratio of the hydrostatic heads of the two liquids in the separating zones being at all times substantially equal to the proportions of the two

liquids in the agitating zones and removing the end product from a settling zone.

2. A process for the treatment of substantially immiscible liquids comprising: flowing a tertiary-base olefine-containing fluid and an acid in counter-current through a series of alternate agitating and settling zones each agitating zone being in communication with no more than two settling zones, the ratio of the hydrostatic heads of the two liquids in the separating zones being at all times substantially equal to the proportions of the two liquids in the agitating zones and removing the dissolved tertiary-base olefine from an end settling zone.

3. A process for the treatment of substantially immiscible liquids comprising: flowing a mineral oil fraction containing olefines in counter-current with an acid through a series of alternate agitating and settling zones only the contiguous zones of which are in communication with each other, the ratio of the hydrostatic heads of the two liquids in the separating zones being at all times substantially equal to the proportions of the two liquids in the agitating zones and removing the treated material from a settling zone.

4. A process for the treatment of substantially immiscible liquids comprising: flowing a mineral oil fraction containing olefines in counter-current with an acid through a series of alternate agitating and settling zones each agitating zone being in communication with no more than two settling zones, the ratio of the hydrostatic heads of the two liquids in the separating zones being at all times substantially equal to the proportions of the two liquids in the agitating zones and removing the absorbed tertiary-base olefines from an end settling zone.

5. A process for the treatment of substantially immiscible fluids comprising: flowing a mineral oil fraction consisting essentially of hydrocarbons containing more than three carbon atoms to the molecule and also containing the corresponding tertiary-base olefines in counter-current with an acid through a series of alternate agitating and settling zones only the contiguous zones of which are in communication with each other, the ratio of the hydrostatic heads of the two liquids in the separating zones being at all times substantially equal to the proportions of the two liquids in the agitating zones and removing the absorbed tertiary-base olefines from an end settling zone.

6. A process for the treatment of substantially immiscible liquids comprising: flowing a mixture of paraffin and olefine hydrocarbons consisting essentially of hydrocarbons containing more than three carbon atoms to the molecule and also containing the corresponding tertiary-base olefines in counter-current with an acid through a series of alternate agitating and settling zones each agitating zone being in communication with no more than two settling zones, the ratio of the hydrostatic heads of the two liquids in the settling zones being at all times substantially equal to the proportions of the two liquids in the agitating zones and removing the absorbed tertiary-base olefines from an end settling zone.

7. A process for the treatment of substantially immiscible fluids comprising: flowing a hydrocarbon mixture containing isobutylene in counter-current with  $H_2SO_4$  through a series of alternate agitating and settling zones only the contiguous zones of which are in communication with each other, the ratio of the hydrostatic heads of the two liquids in the separating zones being at

all times substantially equal to the proportions of the liquids in the agitating zones and removing the absorbed isobutylene from an end settling zone.

8. A process for the treatment of substantially immiscible fluids comprising: flowing a hydrocarbon mixture consisting essentially of  $C_4H_{10}$  and  $C_4H_8$  and containing isobutylene in counter-current with  $H_2SO_4$  through a series of alternate agitating and settling zones each agitating zone being in communication with no more than two settling zones, the ratio of the hydrostatic heads of the two liquids in the separating zones being at all times substantially equal to the proportions of the two liquids in the agitating zones and removing the absorbed isobutylene from an end settling zone.

9. A process for the treatment of substantially immiscible fluids comprising: flowing a hydrocarbon mixture containing isobutylene in counter-current with 65% to 75%  $H_2SO_4$  through a series of alternate agitating and settling zones only the contiguous zones of which are in communication with each other at a temperature below that at which polymerization of secondary-base butylene takes place, the ratio of the hydrostatic heads of the two liquids in the separating zones being, at all times substantially equal to the proportions of the two liquids in the agitating zones and removing the absorbed isobutylene from an end settling zone.

10. A process for the treatment of substantially immiscible fluids comprising: flowing a hydrocarbon mixture consisting essentially of  $C_4H_{10}$  and  $C_4H_8$  and containing isobutylene in counter-current with 65% to 70%  $H_2SO_4$  through a series of alternate agitating and settling zones each agitating zone being in communication with no more than two settling zones at a temperature below that at which polymerization of secondary-base butylene takes place, the ratio of the hydrostatic heads of the two liquids in the separating zones being at all times substantially equal to the proportions of the two liquids in the agitating zones and removing the absorbed isobutylene from an end settling zone.

11. A process for the treatment of substantially immiscible fluids comprising: maintaining at a substantially constant level the height of an acid layer in a settling zone which also contains an olefine-containing fluid substantially immiscible with said acid, agitating the two liquids in a mixing zone which is in communication with only two contiguous settling zones, the ratio of the hydrostatic heads of the two liquids in the settling zone being at all times substantially equal to the proportions of the two liquids in the mixing zone and hydrostatically controlling the flow of fluid from the settling zone to the mixing zone and vice versa while continuously feeding the immiscible fluids to the treating zones in counter-current.

12. A process for the treatment of substantially immiscible fluids comprising: maintaining at a substantially constant level the heights of acid layers in a series of horizontally arranged settling zones which also contain olefine-containing fluid substantially immiscible with said acid, continuously agitating the two liquids in a series of mixing zones alternately disposed with respect to the settling zones and in communication with no more than two settling zones, the ratio of the hydrostatic heads of the two liquids in the settling zones being at all times substantially equal to the proportions of the two liquids in the mix-

ing zones and hydrostatically controlling the flow of fluid from the settling zones to the mixing zones and vice versa while continuously feeding the immiscible fluids to the treating zones in counter-current.

13. A process for the treatment of substantially immiscible fluids comprising: maintaining at a substantially constant level the heights of acid layers in a series of horizontally arranged settling zones which also contain tertiary-base olefine-containing fluid substantially immiscible with said acid, continuously agitating the liquids in a series of mixing zones alternately disposed with respect to the settling zones and in communication with no more than two settling zones, the ratio of the hydrostatic heads of the two liquids in the settling zones being at all times substantially equal to the proportions of the two liquids in the mixing zones and hydrostatically controlling the flow of fluid from the settling zones to the mixing zones and vice versa while continuously feeding the immiscible fluids to the treating zones in counter-current.

14. A process for the treatment of substantially immiscible fluids comprising: maintaining at a substantially constant level the heights of  $H_2SO_4$  layers in a series of horizontally arranged settling zones which also contain tertiary-base olefine-containing fluid substantially immiscible with the  $H_2SO_4$ , continuously agitating the liquids

in a series of mixing zones alternately disposed with respect to the settling zones and in communication with no more than two settling zones, the ratio of the hydrostatic heads of the two liquids in the settling zones being at all times substantially equal to the proportions of the two liquids in the mixing zones and hydrostatically controlling the flow of fluid from the settling zones to the mixing zones and vice versa while continuously feeding the immiscible fluids to the treating zones in counter-current.

15. A process for the treatment of substantially immiscible fluids comprising: maintaining at a substantially constant level the heights of  $H_2SO_4$  layers in a series of horizontally arranged settling zones which also contain isobutylene-containing fluid substantially immiscible with the  $H_2SO_4$ , continuously agitating the liquids in a series of mixing zones alternately disposed with respect to the settling zones and in communication with no more than two settling zones, the ratio of the hydrostatic heads of the two liquids in the settling zones being at all time substantially equal to the proportions of the two liquids in the mixing zones and hydrostatically controlling the flow of fluid from the settling zones to the mixing zones and vice versa while continuously feeding the immiscible fluids to the treating zones in counter-current.

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