

Dec. 7, 1943.

E. E. WILLAUER
REFINING OF MINERAL OILS

2,336,205

Filed Dec. 20, 1940

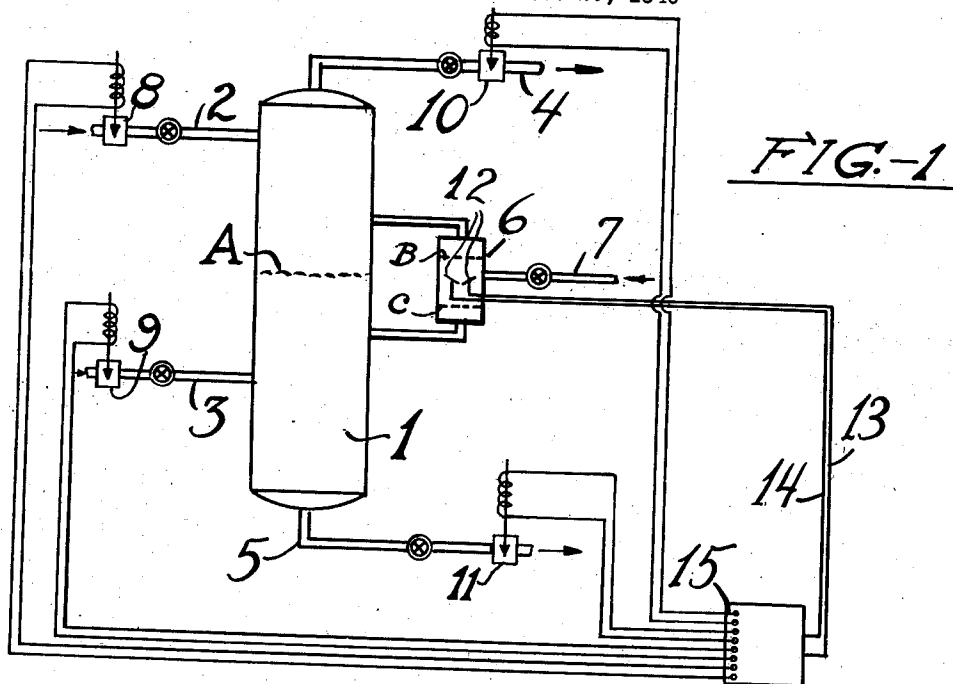


FIG. -1

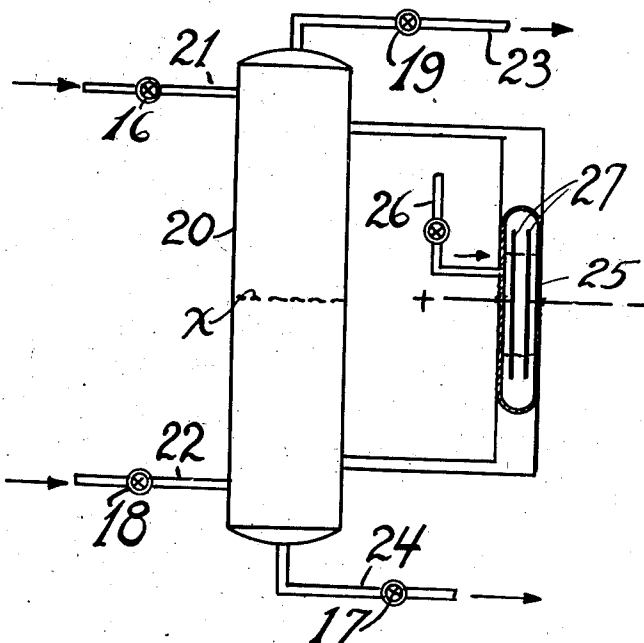


FIG. -2

Earl E. Willauer Inventor
By *P. H. Young* Attorney

UNITED STATES PATENT OFFICE

2,336,205

REFINING OF MINERAL OILS

Earl E. Willauer, Cranford, N. J., assignor to
Standard Oil Development Company, a corporation of Delaware

Application December 20, 1940, Serial No. 370,984

8 Claims. (Cl. 196—13)

The present invention relates to the refining of mineral oils and is more particularly concerned with an improved method for controlling the level of the interface between two fluid phases of different electrical resistances in various refining operations, as for example in solvent treating operations. In accordance with the present invention a third liquid phase, other than the phases between which the control is to be maintained, is employed. For purposes of description the phases between which control is to be maintained are termed the "primary phases" while the third liquid phase utilized in securing the control in accordance with the present invention is termed the "controlling phase." This third liquid phase or controlling phase has a higher conductivity and is substantially immiscible with either of the primary phases. The controlling phase also has an intermediate specific gravity and is employed in a sidearm in an electrical circuit which actuates a control valve in a manner to control the interface level between the primary phases in the main system. In accordance with a preferred modification of the invention, the controlling phase is employed in the electrical circuit in conjunction with plate or strip electrodes in a manner adapted to actuate a rate of flow control valve which responds to the variations in the electrical circuit.

It is known in the refining art to employ two liquid phases under conditions in which it is desirable to control the level at which the interface between the respective phases is maintained. For example, it is known in the art to treat petroleum oils and the like with various selective solvents which have the ability to segregate these oils into the respective constituents as measured by a difference in their chemical and physical properties. The solvent or solvent mixtures usually employed are selected from the class of solvents which have a preferential selectivity for the relatively more aromatic or hydrogen-poor constituents as compared to the relatively more paraffinic or hydrogen-rich constituents. Solvents of this class are, for example, phenol, furfural, sulfur dioxide, cresol, nitrobenzene, aniline, beta beta' dichlorodiethyl ether, and the like. It is also known to use these solvents in combination with other substances, as for example, in combination with liquid normally gaseous hydrocarbons, such as propane and the like. Although a batch or semi-batch operation is entirely satisfactory, the usual practice is to contact the oil and solvent in a countercurrent tower treating process. In this type of operation the heavier

phase, usually the solvent, is introduced into the top of the countercurrent treating tower while the lighter phase, usually the oil, is introduced into the bottom or center section of the tower.

5 These phases flow in a countercurrent relationship. Efficient contact between the countercurrently flowing phases is usually secured by suitable contacting and distributing means, as for example, distributing trays, pierced plates, packed masses, and the like. Conditions are adjusted to form a solvent-poor or raffinate phase, highly paraffinic in nature, and a solvent-rich or solvent extract phase, highly aromatic in nature. The respective phases are separated and the solvent is usually removed from the extract and raffinate phases by distillation. In these processes it is known to handle the raffinate and extract phase by various procedures, for example, the extract phase or the raffinate phase may be cooled before or after removal from the countercurrent treating system thus causing further phase separation. These phases may be removed and handled separately in a manner to produce secondary extract, secondary raffinate which may be removed from the system or returned as reflux to the countercurrent treating tower. In operations of this character it is important to maintain the level of the interface between the two phases in the main extraction zone as well as in the collateral zones at a predetermined point which may vary depending upon the particular operation employed. By suitable adjustment of the oil and solvent feed rate at a temperature below that of complete miscibility, the interface level may be located at either end of or between the ends of the countercurrent treating zone. In countercurrent extractions with solvents heavier than oil, that portion of the treating zone above the interface will be continuous with respect to oil phase and will contain dispersed solvent phase, whereas in that portion below the interface this relationship of the phases will be reversed. The exact position of the interface will be important in insuring that oil and solvent flow countercurrently since, in general, maximum allowable oil thru-puts will be improved by shifting the position of the interface toward the tower top. Furthermore, in order to increase the flexibility of the equipment in order to secure optimum operating conditions for various feed stocks and modes of operation, it is sometimes desirable to change the interface level over a relatively wide range.

Various methods have been proposed for controlling the interface level at a predetermined point. A number of the methods suggested op-

erate upon the differential in the electrical resistivities of the two countercurrently flowing phases. One method which depends upon the difference in resistivity of the liquid phase utilizes a control instrument in an electrical circuit in conjunction with plate or strip electrodes and an electric valve controlling the rate of underflow from the tank or tower. In the control instrument use, the resistance existing between the electrode points is incorporated in the grid circuit of a suitable electron tube. Although the common vacuum or radio tube can be employed in this service, the gas-filled grid-controlled rectifier tube (e. g., Thyatron) is the more appropriate since it allows either full current or no current at all to flow without any intermediate values, thus providing a positive control of the electric valve. In the actual operation, when the phase of highest conductivity builds up to a point where the electrodes are covered, the decrease in resistivity across the electrodes causes the "Thyatron" grid to become less negative in potential with respect to the cathode and the tube to "break down," permitting current to flow through the tube to the valve or to a relay operating the valve. The interface level is then lowered until a phase of higher resistivity covers the electrodes causing the above operation to be reversed.

These methods are not entirely satisfactory due to the low conductivity of the respective phases which results in a decrease in the sensitivity of the level control instrument and results in difficulties in securing a throttling action on the control valve with recurrent loss of the interface level. I have now found a process by which it is possible to efficiently control the interface level between two countercurrently flowing phases which have relatively high electrical resistivities. My process utilizes a third liquid phase or controlling liquid phase which is characterized by having an intermediate specific gravity, a higher electrical conductivity and which is substantially immiscible with the primary phases. The controlling liquid phase is employed in a sidearm arrangement with respect to the main treating zone. My invention may be readily understood by reference to the attached drawing illustrating modifications of the same.

For purposes of description, the invention is described as adapted to a countercurrent solvent treating operation. Figure 1 illustrates an adaptation of my invention employing two electrical contact points, while Figure 2 illustrates the adaptation when employing strip or plate electrodes.

Referring specifically to Figure 1, the selective solvent is introduced into treating zone 1 which preferably comprises a countercurrent solvent treating tower, by means of feed line 2. The solvent flows downwardly through treating zone 1 and countercurrently contacts upflowing oil which is introduced into treating zone 1 by means of feed line 3. Temperature and pressure conditions are adjusted to secure the formation of a raffinate phase and a solvent extract phase. Under the operation as disclosed, the raffinate phase is withdrawn from the countercurrent treating zone 1 by means of line 4 and handled in any manner desirable while the solvent extract phase is withdrawn by means of line 5 and similarly handled. In accordance with the present invention countercurrent treating zone 1 contains a sidearm arrangement 6 into which

the controlling liquid phase is introduced by means of line 7. The controlling phase introduced by means of line 7 is characterized by having a specific gravity intermediate to the countercurrently flowing primary phases. The controlling liquid introduced by means of line 7 also has a higher electrical conductivity and is substantially immiscible in the countercurrently flowing primary phases. Under these conditions three interface levels will exist, that is, an interface level A in the main countercurrent treating zone, an interface level B and an interface level C in the sidearm arrangement 6. An arrangement of this character utilizing a third liquid phase having a relatively high electrical conductivity permits the ready transmittal of electrical impulses to a control valve arrangement which may be adapted to regulate the rate of flow of feed lines 2 and 3 or withdrawal lines 4 and 5 by means of valves 8, 9, 10 and 11 respectively.

Although various means may be employed for securing the desired control, a satisfactory means comprises the following:

Electrical contact points 12 are rigidly attached to the inside walls of sidearm arrangement 6 and are suitably insulated from the arrangement. When the resistance between the electrodes is relatively low, which is secured by having the third controlling phase between the electrodes of a relatively high conductivity, the electric impulses transmitted through lines 13 and 14 to control valve arrangement 15 are relatively constant. However, when the level drops or rises to a point at which the third phase is no longer between the respective electrodes, the electrical resistance between the respective electrodes increases, which materially affects the electrical impulses transmitted to control arrangement 15. The change in electrical impulses in control arrangement 15 may be readily adapted by conventional means to readjust the phase level by regulating a feed line or a withdrawal line.

Referring specifically to Figure 2, the selective solvent is introduced into countercurrent treating zone 20 by means of line 21. This solvent flows downwardly through countercurrent treating zone 20 and countercurrently contacts an upflowing oil which is introduced into the system by means of line 22. Temperature and pressure conditions are adjusted to remove overhead by means of line 23 a raffinate phase and to remove by means of line 24 a solvent extract phase. Under the conditions of operation an interface level will form at point X. Countercurrent treating zone 20 has attached thereto a sidearm arrangement. In accordance with the present process, the third phase is introduced into sidearm arrangement 25 by means of line 26, which phase is substantially immiscible with the countercurrently flowing phases, has an intermediate specific gravity, and has a relatively high electrical conductivity. The sidearm arrangement also has two electrical strip electrodes 27 and is adequately insulated in a manner to transmit electrical impulses without the arrangement 25. Thus as the interface level varies in the main treating zone 20, the respective interface levels in sidearm arrangement will likewise vary and the difference in electrical conductivity between the respective electrodes will be transmitted without the arrangement. A control valve arrangement, similar to that described with respect to Figure 1, is also adapted in a manner to con-

trol valves 16, 17, 18 and 19 on the respective inlet and outlet lines.

The process of the present invention may be widely varied. The invention essentially comprises using a third liquid phase in conjunction with the primary phases in treating operations. This third liquid phase is characterized by being substantially immiscible with the primary phases, has a relatively high electrical conductivity and has a specific gravity intermediate the specific gravity of the primary phases.

Although the invention may be adapted to any refining operation, it is particularly desirable in an operation in which a petroleum oil is treated with a selective solvent such as phenol. Under these conditions, a third phase will preferably comprise a weak solution of an inorganic salt or acid in water. A 0.1 to 0.2 normal hydrochloric acid solution has been found particularly suitable in this capacity. The hydrochloric acid, in addition to markedly increasing the conductivity differential between the third phase and the countercurrently flowing phases, considerably reduces the solubility of water in phenol.

In general, solutions of highly ionizable salts, bases and acids are preferred as the third intermediate liquid phase. The degree of ionization should be in excess of 0.1, preferably in excess of 0.4 or higher. Solutions of satisfactory substances are, for example, hydrochloric acid, nitric acid, sulfuric acid, other acids of sulfur, acids of phosphorus, hydroxides of sodium, potassium, barium, calcium and strontium. Suitable salt solutions are solutions of the metals from the alkaline earth and alkali groups combined with acidic radicals, such as NO_3 , Cl , SO_4 , Br , I , PO_4 , CN and F .

The concentration of the salt, acid and base in the third liquid phase will in general be adjusted to secure the desired electrical conductivity and specific gravity and will be a function of general operating conditions. Usually aqueous solutions will contain from 0.1 to 0.5 weight per cent of these substances.

In order to further illustrate the invention, the following example is given which should not be construed as limiting the same in any manner whatsoever.

EXAMPLE 1

Operations in which various petroleum oil charge stocks are employed result in the following:

Table I

Charge stock (vis.) 210° F.	Treating temp. (°F.)	Specific gravity of un- stripped phases at treat- ing temperature ¹	
		Extract	Raffinate
50.....	120	1.01 to 1.035	0.85 to 0.90
135.....	180	1.00 to 1.02	0.87 to 0.88

¹ Countercurrent treatment of the indicated lube stocks with anhydrous phenol.

The above data indicate that when treating stocks ranging from very light to very heavy lube stocks, a phase having a specific gravity approximating that of water (i. e. any of the very dilute solutions mentioned earlier) will remain fixed in the sidearm attachment.

The following data illustrate the relative electrical conductivities of the various pure liquids entering the extraction system.

Table II

Substance	Conductivity at 25° C. (mho's/cm.)
Petroleum.....	3×10^{-13}
Solvents:	
Phenol.....	1.7×10^{-3}
Nitrobenzene.....	5×10^{-3}
Furfural.....	1.5×10^{-3}
Acetone.....	6×10^{-3}
Acetic acid.....	1.12×10^{-3}
Water (pure).....	4×10^{-3}
KCl (.01 normal soln.).....	1.4×10^{-3}

What I claim as new and desire to protect by Letters Patent is:

1. The process for controlling the interface level between two primary liquid phases in a petroleum oil treating operation, said phases being characterized by having relatively high electrical resistivities which comprises utilizing in said treating operation a third liquid phase which is characterized by having a relatively low electrical resistivity and a specific gravity intermediate the specific gravity of the respective primary phases, maintaining spaced plate electrodes in said third liquid phase, utilizing said third liquid phase in an electrical circuit for transmitting electrical impulses to a control valve arrangement which operates and controls the feed and outlet rates of flow of the said liquids to maintain said third phase between said electrodes.

2. Process as defined by claim 1, in which said third liquid phase comprises an aqueous solution of a highly ionizable substance.

3. Process as defined by claim 1, in which said third liquid phase is maintained in a sidearm arrangement segregated from the main treating system.

4. Process for controlling the interface level between the raffinate phase and the solvent extract phase in a petroleum oil solvent treating operation, said phases being characterized by having relatively high electrical resistivities, which comprises utilizing in said solvent treating operation a third liquid phase which is characterized by having a relatively low electrical resistivity and a specific gravity intermediate the specific gravity of the raffinate phase and the solvent extract phase, maintaining spaced electrodes in said third liquid phase, utilizing said third phase in a circuit for transmitting electrical impulses to control the feed and outlet rates of flow of the liquids to maintain said third phase between said electrodes.

5. Process as defined by claim 4, in which said third phase comprises an aqueous solution of a highly ionizable substance.

6. Process as defined by claim 4, in which said solvent treating operation comprises a petroleum oil solvent treating operation, in which said third phase comprises an aqueous acid solution which is maintained in a sidearm arrangement segregated from the main solvent treating zone.

7. In a process for treating petroleum with another liquid of different density in which the more dense liquid is fed to a treating zone at an upper level and the less dense liquid at a lower level so that the materials flow past one another and form upper and lower layers in the treating zone, the step of controlling the proportions of the two liquids in the said treating zone, which comprises interposing a narrow layer of a third liquid of intermediate density and of greater electrical conductivity than that of the two other

liquids, impressing an electrical potential between fixed electrodes and automatically controlling the proportion of the two organic liquids within the treating zone by adjusting the feed and withdrawal rates of the said liquids by means of the current passing between the electrodes, said current being greater when the liquid of high conductivity closes the circuit between the electrodes than when the circuit is closed by either of the organic liquids.

8. Apparatus for controlling the interfacial level between petroleum and another organic liquid of different densities and high electrical resistance in a treating receptacle with valved inlet and outlet lines for the liquids, which comprises an electrical gauging column connected

with the treating receptacle at both ends, a liquid of low electrical resistance in the gauging column having a density intermediate between the densities of the two organic liquids, spaced electrodes in the gauging column connected electrically to the valves in the lines ancillary to the treating zones whereby the electrical circuit between the electrodes is completed and broken by movement upwardly or downwardly of the liquid of low electrical resistance and whereby the valves in the lines are opened and closed to admit and withdraw the two organic liquids so as to maintain the interfacial level at the desired point in the treating receptacle.

EARL E. WILLAUER.