

May 8, 1945.

B. R. STRICKLAND

2,375,596

REFINING MINERAL OILS

Filed July 16, 1940

2 Sheets-Sheet 1

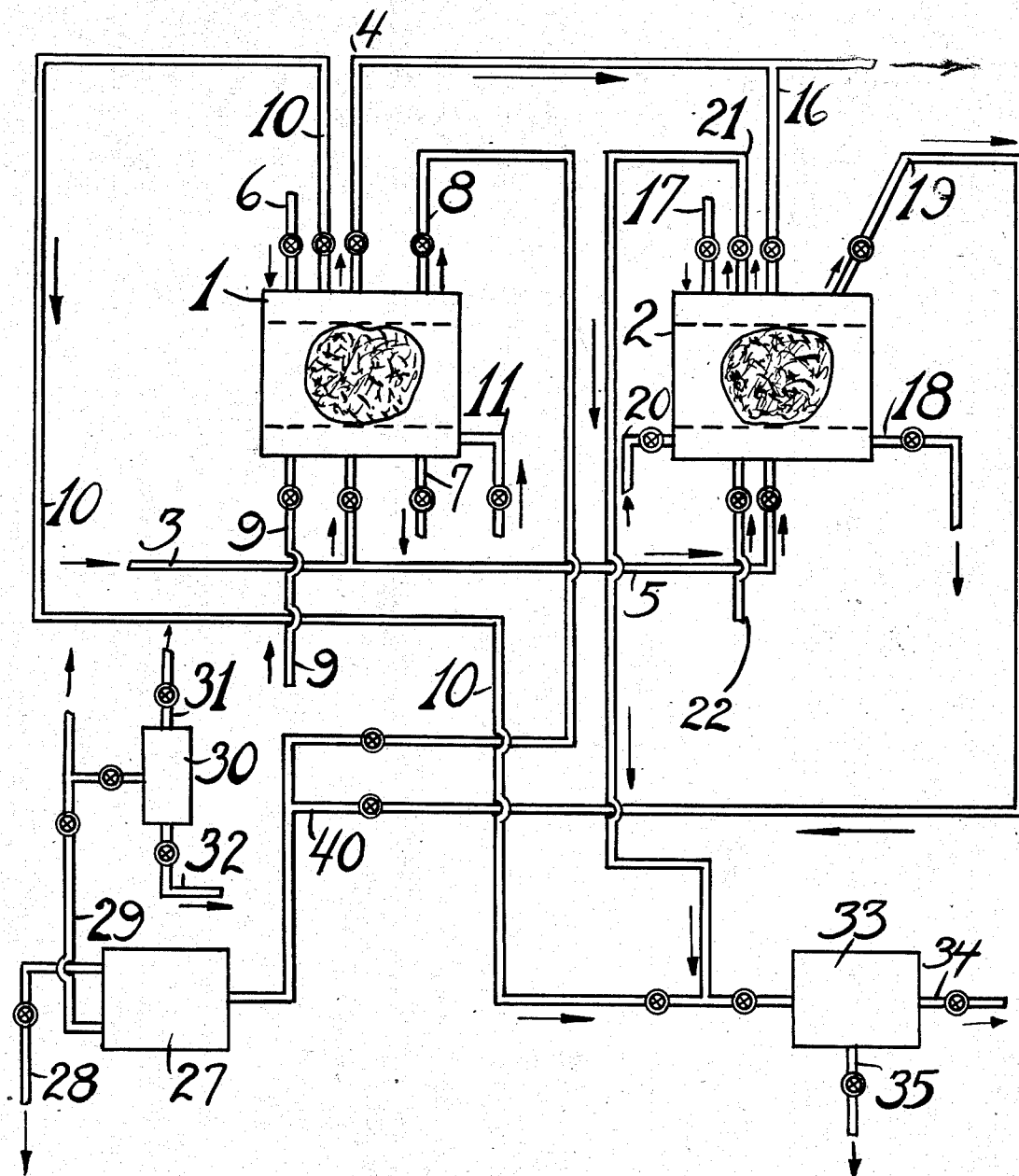


FIG.-1

Barney R. Strickland Inventor
By *A. Young* Attorney

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2 Sheets-Sheet 2

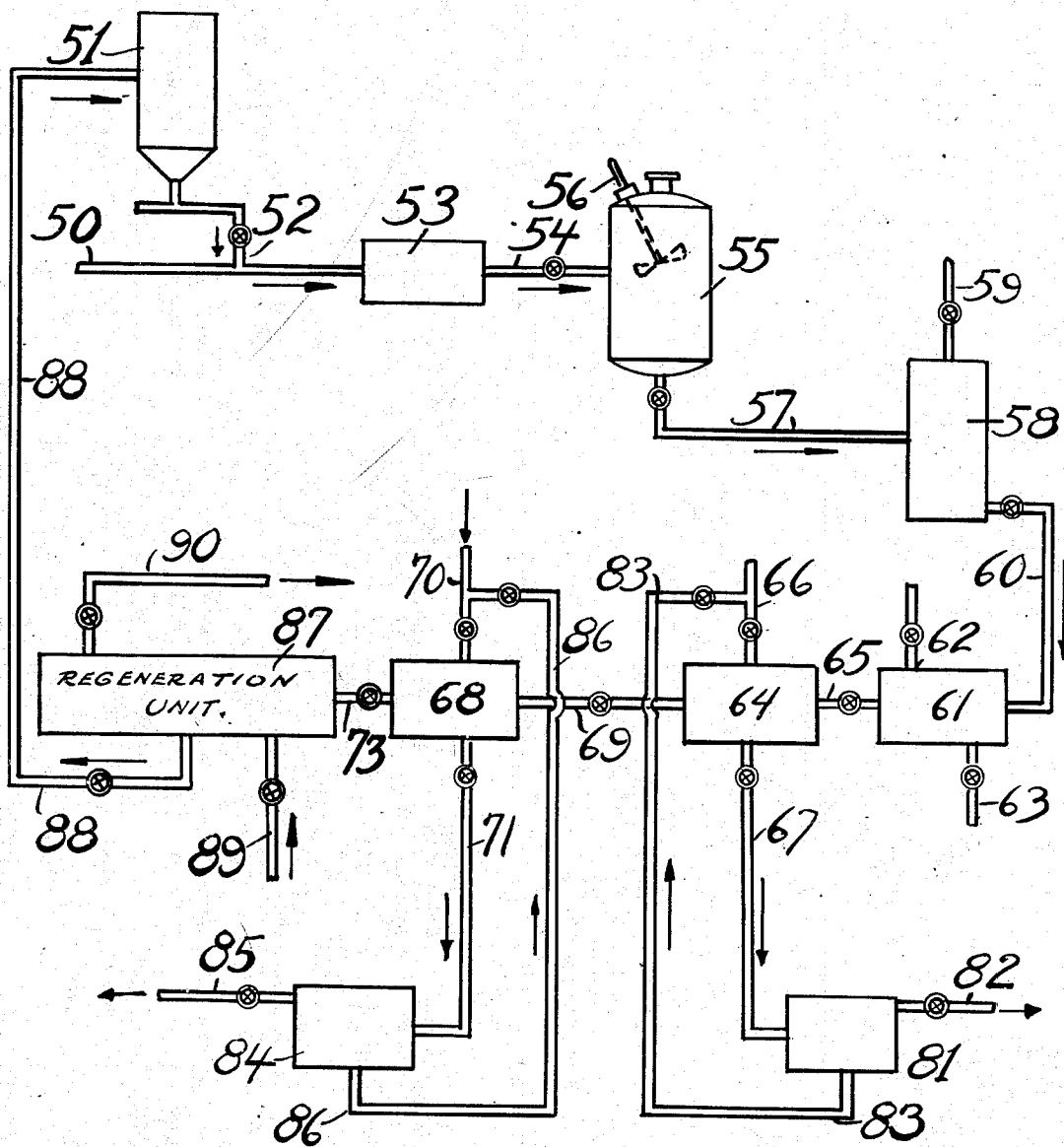


FIG.-2

Barney R. Strickland Inventor
By P. Young Attorney

UNITED STATES PATENT OFFICE

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REFINING MINERAL OILS

Barney R. Strickland, Roselle, N. J., assignor to
Standard Oil Development Company, a corporation of Delaware

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8 Claims. (Cl. 260—514)

The present invention relates to the refining of mineral oils. The invention is especially concerned with the removal, segregation and recovery of naturally occurring acidic oxygen containing compounds from mineral oils containing the same. The invention is particularly concerned with an improved method for the removal and recovery of petroleum oil phenols and petroleum oil naphthenic acids utilizing bauxite. The present invention not only recovers these valuable materials in an efficient and economical manner, but also produces a high quality treated oil product.

It is known in the art to remove and recover petroleum oil phenols, as well as petroleum oil naphthenic acids by various methods since these materials are relatively valuable and are desirable, for example, as inhibiting agents and as intermediate feed products. One method currently employed is to contact the phenol and naphthenic acid containing petroleum oil with various aqueous solutions of alkali metal hydroxides and the like in order to form the corresponding phenolates and naphthenates. These salts are soluble in and are removed with the spent aqueous alkali metal hydroxide solution. The corresponding phenols are recovered from the salts by treating the same with dilute acids and the like in order to form the corresponding phenols or naphthenic acids.

I have now discovered an improved method of removing and recovering these valuable constituents from feed oils containing the same in an efficient manner by which a high yield is secured and which also results in the production of a treated oil product of high quality. In accordance with my invention the mineral oil containing the recoverable phenolic type compounds and naphthenic acids is contacted with bauxite under conditions to substantially, fully remove these constituents from the feed oil. The spent bauxite is handled in a manner to remove, segregate, and recover the phenolic type compounds and naphthenic acids from the bauxite and to fully regenerate or revivify the same. The process of my invention may be readily understood by reference to the attached drawings illustrating modifications of the same.

Figure 1 illustrates a modification of the invention in which the feed oil is passed through a bed of the bauxite, while Figure 2 illustrates another modification in which a slurry of bauxite is utilized. Referring particularly to Figure 1, it is assumed that the phenolic type constituent and naphthenic acid containing feed oil is a petroleum oil boiling in the kerosene oil boiling range. It is to be understood that any number of units may

be utilized and may be arranged in any desirable manner. The feed oil is introduced into initial contacting unit 1 by means of feed line 3. This material flows upwardly through unit 1 and contacts a bed of bauxite which preferably comprises a small particle size so that a large surface area is secured. Temperature and pressure conditions are adjusted in a manner to substantially completely remove the phenols and naphthenic acids from the feed oil. The feed oil is withdrawn from initial contacting unit 1 by means of line 4, withdrawn from the system and handled in any manner desirable. At the end of a fixed time period in which the effectiveness of the bauxite is decreased to a predetermined efficiency, the feed oil is passed into secondary bauxite contacting unit 2 by means of line 5 and withdrawn by means of line 16. The bauxite in contacting unit 1 containing the absorbed phenols and naphthenic acids is handled in a manner to remove and segregate these compounds and to regenerate the bauxite. This is preferably accomplished by washing the bauxite with suitable solvents. For the purposes of description it is assumed that the bauxite is initially contacted with a relatively low boiling petroleum oil distillate solvent having a preferential solubility for the petroleum oil remaining in the bauxite bed. This petroleum oil washing solvent may be introduced by means of line 6 and withdrawn by means of line 7. The bauxite bed is then contacted with a solvent having a preferential selectivity for the phenolic type compounds which for the purposes of description is taken to be water. The water is introduced into initial contacting plant 1 by means of line 9 and withdrawn by means of line 8. Sufficient water is introduced at a temperature and pressure which is adapted to substantially fully remove the phenols from the spent bauxite bed. The bauxite bed, free of petroleum oil and adsorbed petroleum phenols, is contacted with a solvent having a preferential selectivity for the naphthenic acid compounds.

For the purposes of illustration, this solvent is taken to be a 5% sulfuric acid solution which is introduced by means of line 11 and withdrawn by means of line 10. The bauxite bed is treated in a manner to fully regenerate the same. This is preferably accomplished by heating the same to a temperature in the range above 500° F., preferably to a temperature in the range from about 600° F. to 800° F. This may be accomplished by any suitable means, such as superheated steam and the like. At the end of the cycle in which the efficiency of the bauxite in contacting unit 2 drops to a certain predeter-

mined point, the feed oil is again passed into the regenerated bauxite in unit 1. The bauxite-contacted oil is withdrawn from contacting unit 2 by means of line 16, withdrawn from the system, and handled as desired. The bauxite in contacting unit 2 containing the adsorbed phenols and naphthenic acids, is handled in a manner similar to that described with respect to unit 1 in a manner to remove and segregate the phenols and naphthenic acids and to regenerate the bauxite. This is accomplished by initially washing the bauxite bed with a relatively low boiling petroleum solvent introduced by means of line 17 and withdrawn by means of line 18, removing the phenolic type constituents by contacting the bauxite with a preferential solvent for the phenolic type compounds which is introduced by means of line 20 and withdrawn by means of line 19. This solvent preferably comprises water. The naphthenic compounds are removed by contacting the bauxite bed with a dilute acid solution which is introduced by means of line 22 and withdrawn by means of line 21. The bauxite bed is regenerated in a manner described above. The aqueous solution of phenols which is removed from the respective contacting units by means of lines 8 and 19 is introduced into phenol recovery unit 27. In this unit, when treating relatively high boiling petroleum oils the relatively high boiling phenols will separate from the aqueous layer. The phenol layer is withdrawn from the phenol recovery unit 27 by means of line 28, while the aqueous layer is withdrawn by means of line 29 and preferably recycled as described as a phenolic solvent to the system. As the petroleum oil contacted is a relatively wide boiling fraction and contains relatively low boiling and relatively high boiling petroleum phenols, it may be desirable to fully recover the relatively low boiling phenols from the aqueous layer by distilling the same prior to returning the aqueous layer as solvent to the bauxite contacting units. This is accomplished by passing the aqueous layer to still 30, under operating conditions to remove overhead the aqueous layer by means of line 31, and to remove as the bottoms the relatively low boiling phenolic constituents by means of line 32.

The acid solvent containing the naphthenic constituents, removed from the respective contacting plants by means of lines 10 and 21, respectively, is similarly handled in a manner to segregate the naphthenic acids. The acid solvent is introduced into naphthenic acid recovery plant 33 in which a layer separation will occur between the acid solution and the naphthenic acids. The naphthenic acids are removed by means of line 34 and further refined as desired, while the aqueous acid layer is withdrawn by means of line 35 and preferably recycled as acid solvent to the contacting plants as described.

Referring specifically to Figure 2, feed oil is introduced into the system by means of line 50. The feed oil is mixed with a quantity of bauxite which for purposes of illustration is taken to be powdered bauxite and which is introduced from bauxite bin 51 by means of screw conveyor 52. The oil and the bauxite are passed through mixer 53 and passed as a slurry by means of line 54 into agitating plant 55 which may comprise any suitable number of agitating units arranged in any desirable manner. Complete mixing is secured by means of agitator 56. This mixture is withdrawn from plant 55 by means of line 57 and introduced into settling unit 58. The

separation of the solid phase from the liquid phase may be facilitated by any desirable means such as baffles, settling means, and the like. The treated oil is withdrawn from unit 58 by means of line 59 and handled in any desirable manner. The bauxite containing adsorbed thereon the phenolic type compounds and naphthenic acids is withdrawn from unit 58 by means of line 60 and handled in a manner to remove and recover the phenols and naphthenic acids and to substantially fully regenerate the bauxite. This is preferably accomplished by passing the bauxite to washing unit 61 in which the occluded relatively high boiling petroleum oil constituents are removed by washing with a relatively low boiling petroleum oil solvent which is introduced by means of line 62 and withdrawn by means of line 63. The washed bauxite is introduced into phenol recovery unit 64 by means of line 65, in which the phenols are removed by contacting the bauxite with a solvent having a preferential solubility for phenolic type compounds. For the purposes of illustration it is assumed that the solvent comprises water which is introduced by means of line 66 and withdrawn by means of line 67. The bauxite is passed to naphthenic acid recovery unit 68 by means of line 69 in which the naphthenic acids are removed from the bauxite by contacting with a suitable solvent which for the purposes of description is assumed to be a dilute acid solution which is introduced by means of line 70 and withdrawn by means of line 71. The bauxite, free of adsorbed phenolic type compounds and naphthenic acid type constituents, is handled in a manner to substantially fully regenerate the same. The bauxite is withdrawn by means of line 73, passed to regeneration unit 87, wherein the bauxite is heated to the desired temperature, withdrawn by means of line 88 and recycled to the system as described. Superheated steam may be introduced into regeneration unit 87 by means of line 89 and withdrawn by means of line 90. It is to be understood that other equivalent heating means may be employed. The aqueous solution of phenol, withdrawn from unit 64 by means of line 67 is passed to phenol recovery unit 81 in which a layer separation occurs between the relatively high boiling phenols and the aqueous solution. The relatively high boiling phenols are withdrawn by means of line 82, while the aqueous solution is withdrawn by means of line 83 and recycled to unit 64. The phenolic layer is withdrawn by means of line 82, distilled or further refined in any manner desirable. Under certain conditions when the petroleum oil treated is of a relatively wide boiling range and the aqueous solution contains relatively low boiling soluble phenols, it may be desirable to distill the aqueous solution withdrawn from recovery unit 81 in order to remove the relatively low boiling phenols prior to recycling the aqueous solution to unit 64. The acid solution containing the naphthenic acids withdrawn from unit 68 by means of line 71 is passed to naphthenic acid recovery unit 84 in which a layer separation occurs between the naphthenic acids and the dilute acid solution. The naphthenic acids are withdrawn from the system by means of line 85, distilled or further refined in any manner desirable. The dilute acid solution is withdrawn from unit 84 by means of line 86 and recycled to unit 68.

The processes of the present invention may be widely varied. Although the method may be employed for the recovery and segregation of

phenolic type constituents and naphthenic acids from any feed oil, it is particularly applicable in the recovery of relatively high boiling petroleum phenols and petroleum naphthenic acids from petroleum oils boiling in the gas oil and lubricating oil boiling range. These substances, due to their characteristics, have heretofore been relatively difficult to segregate.

The bauxite preferably comprises a native aluminum hydroxide containing from 50% to 70% of Al_2O_3 and from 25% to 30% of water. In general it is preferred that the bauxite be activated by burning the same at a temperature above about 500° F. to 900° F., preferably at a temperature from about 600° F. to 800° F.

The operating conditions likewise may be widely modified. The flow of the respective treating agents may be either upflow or downflow. Temperatures and pressures may vary and will depend upon the particular feed oil being treated, the quantity and character of the phenols and naphthenic acids present, as well as upon the particular bauxite being used and upon the feed rates and particle size. In general it is preferred to employ atmospheric temperatures and pressures, although temperatures in the range from about 30° F. to 250° F. may be employed in particular instances. If the petroleum oil be of a relatively high viscosity, it may be desirable to employ heating means or to dilute the oil with an inert dilution solvent, as for example a relatively low boiling petroleum oil or with a relatively low boiling hydrocarbon constituent. The feed rates may vary considerably depending upon the general operating conditions, the character of the feed oil being treated, as well as upon the type of bauxite being employed. When the process comprises the utilization of stages, feed rates are in the general range from one to seven volumes of oil per volume of bauxite per hour. The preferred rates are from two to four volumes of oil per volume of bauxite per hour. When employing a slurry, the amount of slurry is preferably in the range from one volume of bauxite per fifteen to twenty-five volumes of oil.

Although it is not essential, it is preferred that the bauxite after contact with the oil be washed with a solvent which will remove occluded oil portions from the bauxite prior to treating the bauxite to remove the adsorbed phenols and naphthenic acids. This solvent may be any relatively low boiling hydrocarbon. A desirable material comprises naphtha boiling in the range from about 300° F. to 420° F.

The phenols are preferably removed from the bauxite by treating with water at normal temperatures and pressures. The amount of water employed may vary widely depending upon the quantity of phenols present and the particular bauxite employed. In general it is preferred to employ from about one to four volumes of water per volume of bauxite in order to displace the phenolic type constituents. A preferred modification of utilizing water at normal temperatures and pressures for the displacement of the phenolic type constituents is to agitate the mass with air or a similar agitating means. Under certain conditions it may be desirable to employ heated water or steam in order to remove the phenols, although in general this method is not preferred. If steam be employed in order to remove the phenols, it is preferred that the steam operation be conducted at a temperature in the range from about 600° F. to 800° F. The aqueous solution, after removal from the bauxite bed, will form

two phases comprising a phenol phase and an aqueous phase. The phenol phase is separated and may be further refined in any manner desirable. Although the aqueous phase may be distilled in order to remove any relatively low boiling soluble phenolic type compounds present, it is preferred to recirculate the same as a phenol solvent directly to the bauxite contacting units.

The acid solution employed for the removal of the naphthenic type constituents from the bauxite may vary considerably. Any mineral acid may be employed, although in general it is preferred to utilize a dilute sulfuric acid having an acid concentration in the range from about 2% to 10%. A particularly desirable solvent for removing naphthenic type constituents from the bauxite comprises a 5% sulfuric acid solution. This solution, after the removal of the naphthenic acid constituents, is likewise preferably recycled to the system as described.

The spent bauxite, free of naphthenic acid and phenolic type constituents, may be handled in any suitable manner in order to regenerate the same. Although the spent bauxite, free of the phenols and naphthenic acid constituents may be regenerated in any satisfactory manner, it is preferred that the bauxite be regenerated by heating the same to a temperature in the range from about 600° F. to 900° F., preferably in the range from about 600° F. to 700° F. The heating of the bauxite may be accomplished by any suitable means, but is preferably accomplished by means of superheated steam.

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

Example 1

A naturally occurring bauxite of a particle size in the range from 30 to 60 mesh was heated at 800° F. to 900° F. A petroleum oil boiling in the kerosene boiling range and containing about 0.2% phenols and naphthenic acids was filtered through the bauxite at a rate of one volume of oil per volume of bauxite per hour at room temperatures and at atmospheric pressures. It was found that the bauxite contacted oil was substantially completely free of phenols and naphthenic acids. The spent bauxite was contacted with light naphtha in order to remove the residual petroleum oil. The bauxite was contacted with wet steam which removed phenols, and then contacted with a dilute acid solution in a manner to remove the naphthenic acids.

Example 2

A portion of spent bauxite employed in the removal of phenols and naphthenic acids from petroleum oils boiling in the kerosene range was steamed with wet steam and finally treated with super-heated steam at 500° F. It was found that this operation removed the adsorbed phenols. Another portion of the bauxite was steamed at 600° F. to 660° F. This treatment practically completely regenerated the bauxite and completely removed the adsorbed phenols.

Example 3

Various portions of bauxite were subjected to heat treatments at different temperatures. It was found that a critical temperature range existed in the range from about 600° F. to 800° F. Temperatures below about 500° F. are ineffective. The following data demonstrates the effective-

ness of different portions of bauxite activated at various temperatures. The relative effectiveness of the respective portions is measured by the quantity of petroleum oils which could be completely free of phenolic type constituents.

Temperature of activation, °F.---	500	600	700	800	900	1,200	1,600
Volumes of phenol-free petroleum oil/vol. of bauxite produced----	2	43	47	37	38	27	21

Example 4

A spent bauxite containing adsorbed phenols was treated with several volumes of water per volume of bauxite. A brown phenolic oil layer was separated which contained approximately 18% phenols expressed as tertiary amyl phenol. Another portion of the spent bauxite utilized for the separation of phenolic type constituents from a petroleum oil boiling in the kerosene boiling range was heated for about ten minutes at 300° F. in an autoclave with five volumes of water per volume of bauxite. A brown phenolic oil layer separated, which contained about 12% phenols expressed as tertiary amyl phenol.

Apparently the bauxite of the present invention reacts with the naturally occurring acidic oxygen containing compounds to form reaction products which may be readily regenerated from the bauxite. The regeneration operation may be controlled in a manner to preferentially first regenerate the phenolic type constituents which may be separated. After separation of the phenolic type constituents the naphthenic acid constituents may be readily regenerated and separated.

The process of the present invention is not to be limited by any theory or mode of operation but only by the following claims in which it is desired to claim all novelty insofar as the prior art permits.

I claim:

1. The process for recovering and segregating naturally occurring phenols and naphthenic acids from petroleum oils containing the same which comprises contacting said oils with bauxite whereby phenols and naphthenic acids are adsorbed on the bauxite, removing the oil from the bauxite, treating the bauxite with water thereby selectively removing the phenols from the bauxite, recovering phenols from the aqueous treating liquor, treating the phenol-free bauxite with a dilute acid solution whereby naphthenic acids

are removed from the bauxite, reactivating the water- and acid-treated bauxite and reusing the reactivated bauxite.

2. The process for recovering and segregating naturally occurring phenols and naphthenic

10 acids from petroleum oils containing the same which comprises contacting said oils with bauxite activated at a temperature of from 600 to 800° F. whereby the phenols and naphthenic acids are adsorbed on the bauxite, removing the oil from the bauxite, treating the bauxite with water thereby selectively removing the phenols from the bauxite, recovering phenols from the aqueous treating liquor, treating the phenol-free bauxite with a dilute acid solution whereby the naphthenic acids are removed from the bauxite, reactivating the water- and acid-treated bauxite at a temperature of from 600 to 800° F. and reusing the reactivated bauxite.

3. The process according to claim 2 wherein the bauxite is activated and reactivated with super-heated steam at a temperature of 600 to 800° F.

4. The process for recovering and segregating naturally occurring phenols and naphthenic acids from petroleum oils containing the same which comprises contacting said oils with bauxite whereby phenols and naphthenic acids are adsorbed on the bauxite, removing the oil from the bauxite, treating the bauxite with water thereby selectively removing the phenols from the bauxite, recovering phenols from the treating liquor, treating the phenol-free bauxite with a dilute sulfuric acid having an acid concentration in the range from about 2% to about 10%, thereby removing the naphthenic acids from the bauxite, and reactivating the bauxite.

5. The process according to claim 4 wherein bauxite, activated at a temperature between 600 and 800° F., is used.

6. The process according to claim 1 wherein water is used in the form of wet steam.

7. The process according to claim 2 wherein water is used in the form of wet steam.

8. The process according to claim 4 wherein water is used in the form of wet steam.

BARNEY R. STRICKLAND.