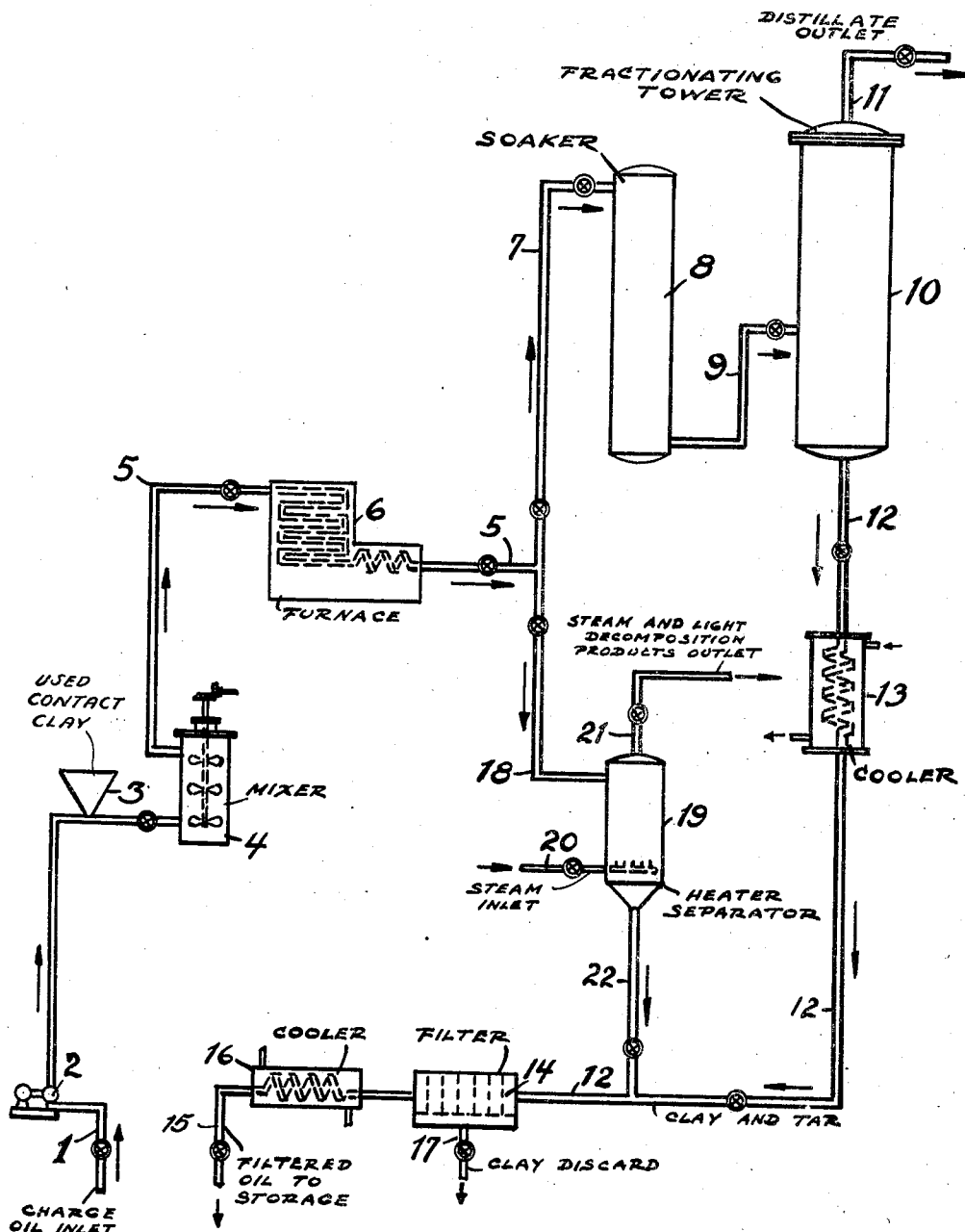


Feb. 8, 1944.

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REFINING OF MINERAL OILS

2,340,939

Filed June 6, 1942



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UNITED STATES PATENT OFFICE

2,340,939

REFINING OF MINERAL OILS

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Application June 6, 1942, Serial No. 446,010

8 Claims. (Cl. 196—35)

The present invention relates to the refining of mineral oils and it relates particularly to a method of removing undesirable alkali and alkali-containing constituents from petroleum oils, especially fuel oils.

It is known in the art to refine petroleum oils by various operations which comprise distillation, cracking and reforming operations, and also to treat the segregated products by various chemical operations in which caustic, sulfuric acid, and various clays and adsorbents are employed. It is also known to employ sludges, distillation residues and other waste products derived from processing naphthas, gas oils, and lubricating stocks in the production of fuel oils of various grades and qualities. Fuel oils are also made from cracked tars, crude residua, and cracked crude residua. Many of the stocks employed in the manufacture of fuel oils contain undesirable alkaline materials such as caustic alkalies, soaps, salts, etc. This is particularly true of crude and lube stock residua. If these alkaline materials are not removed from fuel oils, they will cause difficulties, such as slagging of the brick walls and plugging of the burners, in the operation of furnaces in which the oils are burned. Hence, in order to produce a marketable product, it is essential that undesirable alkaline materials be removed from fuel oils to the extent that the oils are substantially neutral and contain not more than about 0.01 to 0.20 weight per cent of mineral ash, depending upon the particular grade of fuel concerned.

Adsorbents such as colloidal clay, charcoal, fuller's earth, bauxite, etc., have been employed in decolorizing and removing acid bodies from lubricating oils at temperatures below about 450° F. It is also known that a small amount of soaps can be removed from lubricating oils by substantially this same treatment. For instance in U. S. Patent 1,655,068, Weir et al. disclose a process for treating lubricating oil stocks which comprises first treating the oil with sulfuric acid by well known methods and removing the sludge, then neutralizing the acidic oil with a strong

solution of caustic soda sufficient in quantity only to neutralize the acid bodies present without adding a substantial excess of the alkali, subsequently contacting the neutralized oil with a colloidal clay at a temperature of approximately 300° F. and then filtering to remove the clay. In this manner the patentees remove soaps from the lubricating oil by preferential adsorption rather than by water washing since the latter method would result in emulsion difficulties. While these methods of conditioning oils by clay treatment are satisfactory for their purpose, they are not satisfactory for use in removing large quantities of alkaline materials from crude or heavy-distillate residua because they are too inefficient and expensive. This is particularly true where fuel oils of low ash and low alkalinity content are to be produced from highly alkaline stocks, such as the distillation residua derived from either the distillation of a molten alkali treated oil, particularly a lube stock, or the distillation of an oil in the presence of a large excess (based on the neutralization number of the oil) of caustic soda solution.

It has now been discovered that undesirable alkaline materials, that is alkali and alkali-containing constituents, can be removed from mineral oils, particularly fuel oil stocks such as crude residua or lube stock residua, by contacting the mineral oils at temperatures above about 400° F. with a contact clay which has previously been used in decolorizing and removing acid bodies from an acid treated mineral oil, particularly a lube stock. Contact clays which have been used in decolorizing and removing acid bodies from oils which have been treated with acid and the acid sludge settled and removed therefrom, contain adsorbed organic and inorganic constituents which are acidic in nature and which make these clays much more efficient for removing alkaline materials from mineral oils than are fresh contact clays and other common adsorbents. In some instances it has been found that the used contact clays are at least twice as efficient as are fresh contact clays of the same type when com-

pared on an oil-free weight basis. This particular method of removing undesirable alkaline materials from mineral oils is particularly desirable since the high efficiency of the clay reagent permits realization of the maximum capacity of the treating equipment. The reagent is available to many oil refiners at little or no cost and there is little or no loss of oil as "soakage" since the used contact clay is generally already saturated with oil. However, it should be understood that used clays which have had the oil recovered therefrom by solvent extraction methods may be employed in the process of our invention with good results.

In accordance with this invention undesirable alkaline materials are removed from fuel oils, or other oils of similar nature, by contacting the oils at temperatures between about 400° and 1000° F., preferably between about 650° and 900° F., with a contact clay which has previously been used to neutralize and decolorize an acid oil. The time of contact and the quantity of clay necessary to produce the desired results in this process are dependent upon the quantity of alkaline material to be removed from the oil and the treating temperature employed. In general, the higher the treating temperature, the shorter is the time of contact and the smaller is the quantity of clay required to remove a given amount of undesirable alkaline material from the oil being treated. For instance, it has been found that with one stock the clay requirements for treating temperatures in the neighborhood of 400° F. are roughly ten times as great as the clay requirement at temperatures in the vicinity of 800° F. The time of contact between the oil and the clay reagent necessary for removal of undesirable alkaline material may vary between about 1 minute and 120 minutes, the preferred range being between about 10 minutes and 30 minutes; however, where the treat is carried out under cracking conditions it may be desirable to employ longer periods of contact in order to secure the desired amount of cracking of the oil. The quantity of clay employed in this process usually varies between 1 and 10 pounds per barrel of oil; however, in some instances, it may be desirable to employ as much as 40 pounds of clay per barrel of oil, particularly when the oil contains unusually large quantities of alkaline materials, such as might be the case when treating mineral oil residua derived from the distillation of molten-caustic treated lubricating oil stocks. Residua of this type often contain alkali and alkali-containing constituents equivalent to about 5 pounds of NaOH per barrel of oil.

The process of this invention may be readily understood by reference to the attached drawing which illustrates specific embodiments of the same. The charge oil containing excessive amounts of undesirable alkali and alkali-containing constituents is introduced into the system by means of line 1 and pump 2. By means of clay injector 3, contact clay which has previously been used in decolorizing and removing acid bodies from an acid oil is introduced into the charge oil ahead of mixer 4. The oil-clay mixture is thoroughly agitated in mixer 4 before being passed in line 5, through furnace 6, where it is heated to a cracking temperature in the range between about 650° F. and 950° F., preferably about 800° F. The hot oil-clay mixture is passed from line 5 to soaker 8 by means of line 7.

Soaker 8 is a time reaction zone preferably of the type commonly employed in the coil and drum cracking process. The oil-clay mixture is held in soaker 8 under cracking conditions for sufficient time to secure the desired amount of cracking of the oil charge; then the mixture is discharged through line 9 to fractionating tower 10. The oil-clay mixture in heating coil 5 and soaker 8 may be maintained under any desired pressure in the range between about 0 and 1000 pounds per square inch gauge. The preferred pressure is a pressure just sufficient to maintain the desired amount of cracking residue in the liquid phase.

In fractionating tower 10, the light decomposition products are separated from the clay, the heavy decomposition products and the undecomposed oil and removed overhead through line 11. The heavy decomposition products, the undecomposed oil and the clay are withdrawn as a residual mixture from fractionating tower 10 by means of line 12. The residual mixture is cooled to the desired filtering temperature, preferably in the range between about 400° F. and 600° F., by means of cooler 13, in line 12, before being introduced into filter 14.

In filter 14, which may be of any suitable design, the clay and other solid particles are separated from the liquid oil. The filtered oil is cooled by means of cooler 16, located in line 15, before being passed to storage. The clay and other solids removed from the oil in filter 14 are discarded from the system by means of line 17.

The aforescribed operation is preferable where the charge oil is highly viscous and a reduction in viscosity must be effected before the oil can be utilized as fuel oil. However, if the charge oil is of low viscosity and no cracking is required, a slight modification of the aforescribed process is preferable. The modification consists of heating the oil-clay mixture flowing through line 5 in furnace 6 to a desired sub-cracking temperature in the range between about 400° F. and 650° F. and then passing the mixture to heater-separator 19 by means of line 18 instead of passing it to soaker 8 by means of line 7. Heater-separator 19 is preferably a closed drum with means, such as line 20, provided for introducing steam to agitate the oil-clay mixture and to simultaneously strip out any light decomposition products in the oil. The light decomposition products and steam are removed from heater-separator 19 by means of line 21 and the oil-clay mixture is passed to filter 14 by means of lines 22 and 12. The primary purpose of heater-separator 19 is to provide additional time of contact between the oil and the clay over that provided by the heating coil and transfer lines. In some cases, particularly where relatively short contact times are desired and where the heating coil and transfer lines are ample for supplying this time of contact, it may be desirable to pass the hot oil-clay mixture directly from line 5 to filter 14 by means of a line not shown on the drawing.

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

EXAMPLE I

In a regular plant operation, a Coastal crude was distilled in the presence of aqueous caustic

(90% theoretical based on neutralization number) to produce an alkaline residuum representing a yield of about 13% on the crude. While still hot, this alkaline residuum was fluxed with a cracking coal tar in the ratio of 1.5 volumes of residuum to 1 volume of tar to produce a fuel oil sufficiently fluid for pumping at room temperature without encountering excessive pressure drop through the line. Samples of this plant-produced alkaline fuel oil were contacted in the laboratory for about 30 minutes at 400° F. with 0.125, 0.25, 0.50, and 1.0 pound (oil-wet basis) of used decolorizing clay per gallon of oil. This used clay had previously been employed for decolorizing and removing acid bodies from a lubricating oil which had been acid treated in propane solution. After completing the contact operation, the hot oil was filtered through paper to remove the clay therefrom. These clay treated samples of fuel oil were then inspected for ash, sediment by hot filtration, sediment by extraction, and alkalinity. For purpose of comparison, a sample of the alkaline residuum was heated to a temperature above 300° F. in the absence of clay and was then filtered through paper and tested in the same manner as the contacted oils.

The following data were obtained:

Table I

	Sample No.				
	1	2	3	4	5
Clay treat, lbs./gal. oil:					
Oil-wet basis.....	None	0.125	0.25	0.50	1.0
Oil-free basis.....	None	.092	0.19	0.37	0.74
Ash..... weight, percent.....	0.31	0.26	0.20	0.12	0.02
Sediment by hot filtration..... percent.....	0.014	0.02	0.018	0.012	0.00
Sediment by extraction..... do.....	0.02	0.01	0.00	0.00	0.01
Alkalinity..... weight, percent NaOH.....	0.197	0.103	0.082	0.052	0.033
Reduction of ash..... percent.....	16.1	35.5	61.3	93.5	
Reduction of alkalinity..... do.....	47.7	58.4	73.6	80.7	

It will be noted from these data that the used-clay treatment effected a reduction in the ash, and alkalinity of the fuel oil and that this reduction is proportional to the amount of clay employed.

EXAMPLE II

A reduced Coastal crude (48% Btms.) was treated in the liquid phase, at a temperature of 570° F., with an amount of molten anhydrous caustic in excess of 300 per cent based upon the neutralization number of the oil. The molten caustic comprised approximately a eutectic mixture of NaOH and Na₂CO₃. After separating the excess caustic, the treated reduced crude was distilled, taking overhead the desirable lube oils and leaving an alkaline residuum representing a yield of approximately 20% on the crude. This alkaline residuum was divided into several portions which were contacted with various amounts of used clay (the same type of clay described under Example I) for 30 minutes at temperatures of 400° F., 550° F. and 650° F. In each case, the clay was separated from the oil by filtering the mixture through paper while hot. The data secured in this experiment are given in the following table:

Table II

	Sample No.						
	1	2	3	4	5	6	7
Contact temperature° F.....		400	400	550	550	650	650
Clay treat, lbs./gal. oil:							
Oil-wet basis.....	None	0.50	1.0	0.25	0.50	0.10	0.25
Oil-free basis.....		0.37	0.74	0.19	0.37	0.07	0.19
Ash..... weight per cent.....	0.94	0.48	0.39	0.35	0.35	0.89	0.36
Sediment by hot filtration..... per cent.....	0.05	0.0	0.03	0.01	0.06	0.37	0.04
Sediment by extraction..... per cent.....	0.03	0.0	0.02	0.01	0.06	0.45	0.05
Alkalinity..... weight per cent NaOH.....	0.58	0.30	0.18	0.30	0.17	0.30	0.07
Reduction of ash..... per cent.....		48.9	58.5	62.8	62.8	5.3	61.7
Reduction of alkalinity..... per cent.....		48.3	69.0	48.3	74.1	48.3	87.9

These data show that, by employing the higher contact temperatures, lower quantities of clay are required to give a desired improvement in quality of the oil.

EXAMPLE III

Contacting residua at elevated temperatures with clays that have previously been employed in decolorizing and removing acid bodies from acid treated oils becomes less effective as a means of removing undesirable alkaline materials from the oil if the residua are neutralized, such as with dilute sulfuric acid or acid sludge, prior to being treated with the used clay. A comparison of the results obtained in the following experiments with the results given under Examples I and II show this to be true.

In one experiment a sample of the molten-caustic treated residuum described under Example II was neutralized by adding thereto a suitable amount of acid sludge derived from acid treating lubricating oil stocks in propane solution. The sample of neutralized residuum was then divided into three portions. One portion of the residuum was contacted for 30 minutes at 400° F. with 0.25 pound of the used clay described under Example I (oil-wet basis) per gallon of residuum. A second portion of the residuum was contacted under these same conditions of temperature and time with 1.0 pound of the used clay per gallon of residuum. The clay was removed from these contacted portions of residuum by filtering them while hot through paper. Data obtained upon these portions of clay treated oil, together with data obtained upon the third portion of the neutralized residuum which was heated in the absence of clay to a temperature above 300° F. and then filtered through paper, are given in Table III.

In another experiment the plant-produced alkaline fuel oil described under Example I was neutralized in the laboratory with dilute sulfuric acid and then divided into two portions. One portion of the neutralized oil was contacted for 30 minutes at 400° F. with 1.0 pound of the used clay described under Example I (oil-wet basis) per gallon of oil and then filtered through paper. For purpose of comparison, the second portion of neutralized oil was heated to a temperature of about 400° F. in the absence of clay and then filtered through paper. The data obtained on these two samples of oil are also given in Table

III.

Table III

	Neutralized samples of molten-caustic treated residuum			Neutralized samples of plant-produced alkaline fuel oil	
	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5
Contact temperature.....°F.		400	400		400
Clay treat, lbs./gal. oil:					
Oil-wet basis.....	None	0.25	1.0	None	1.0
Oil-free basis.....		0.19	0.74		0.74
Ash.....weight, percent..	1.38	1.14	1.08	0.14	0.09
Sediment by hot filtration, percent..	0.05	0.01	0.045	0.06	0.07
Sediment by extraction.....do.	0.04	0.02	0.03	0.03	0.07
Alkalinity, weight, percent NaOH..	0.03	0.06	0.01	0.15	0.05
Reduction of ash.....percent..		17.4	21.7		35.7
Reduction of alkalinity.....do.		-100.0	66.7		66.7

EXAMPLE IV

The superiority of contact clay which has previously been used in decolorizing and removing acid bodies from acid oils over ordinary adsorbents, specifically fresh contact clay, is clearly demonstrated in the following experiment.

In carrying out this experiment, separate portions of a heavy Coastal crude residuum containing a large amount of undesirable alkaline material were contacted with various amounts of fresh contact clay (Milwhite No. 2) at a temperature of 500° F. for 30 minutes in the presence of steam. Following this same procedure, additional portions of the residuum were contacted with various amounts of extracted and non-extracted spent clay. The term "spent clay" is understood to mean a contact clay which has previously been used in decolorizing and removing acid bodies from an acid treated oil. The terms "extracted" and "non-extracted" imply that oil usually present in spent contact clay has or has not been extracted from the clay by means of a suitable solvent such as propane or naphtha. Data secured here are given in Table IV below:

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EXAMPLE V

A heavy Coastal crude residuum containing a large amount of undesirable alkaline materials was admixed with a contact clay which had previously been used in decolorizing and removing acid bodies from an acid treated lubricating oil, using a ratio of about one-tenth of a pound of clay per gallon of oil. The mixture was placed in a retort and heated to and maintained at a temperature of about 780° F., under a pressure of 25 pounds per square inch gauge and with mechanical agitation, until the quantity of light decomposition products distilling overhead amounted to about one-third the weight of the original oil charge. The mixture of oil and clay was then cooled to a temperature of about 520° F. before being filtered (with vacuum) through a pre-coat filter bed comprising one and one-half inches of diatomaceous earth. Experimental data and properties of the oil before and after subjection to this treatment are given in Table V below.

For purpose of comparison, another portion of a similar heavy Coastal crude residuum was cracked in the absence of the contact clay under

Table IV

	Charge oil	Type of clay used							
		Fresh contact clay			Spent contact clay				
					Extracted		Non-extracted		
		Treat No. 1	Treat No. 2	Treat No. 3	Treat No. 4	Treat No. 5	Treat No. 6	Treat No. 7	Treat No. 8
Contact temp.....°F.		500	500	500	500	500	500	500	500
Clay treat, lbs./gal. oil:									
Oil-wet basis.....		1.0	1.5	2.0	0.5	1.0	1.0	1.5	2.0
Oil-free basis.....							0.74	1.11	1.48
Alkalinity.....weight, percent NaOH..	0.33	0.135	0.085	0.088	0.195	0.08	0.078	0.049	0.044
Ash.....weight, percent..	0.21	0.081	0.055	0.025	0.105	0.05	0.073	0.010	0.012
Neutralization value.....	0.06	0.84	1.37	0.90	0.82	1.59	1.34	1.62	1.27
Sediment by extraction.....percent..	0.02	0.02	0.03	0.02	0.02	0.02	0.03	0.02	0.02
Sediment by hot filtration.....do.	0.06	0.04	0.03	0.02	0.02	0.04	0.02	0.01	0.02
Reduction of alkalinity:									
Percentage.....		59.1	74.2	73.3	40.9	75.8	76.4	85.2	86.6
Percentage/lb. oil-free clay.....		59.1	49.4	36.7	81.8	75.8	103.2	76.8	53.6
Reduction of ash:									
Percentage.....		61.5	73.9	88.1	50.0	76.2	65.3	95.2	94.4
Percentage/lb. oil-free clay.....		61.5	49.3	44.1	100.0	76.2	88.2	85.8	63.8

These data show that the spent contact clay is roughly from one and one-half to two times more efficient than fresh contact clay as a treating reagent for removing undesirable alkaline material from mineral oils.

substantially the same conditions of temperature, pressure and amount of decomposition as previously described. The residual cracked oil was divided into two portions, one being filtered

75 through a bed of diatomaceous earth and the

other not being filtered. Experimental data and the properties of the oil before and after the cracking treatment are given in Table V.

Table V

	Cracked with clay	Cracked without clay
Clay treat, lbs./gal. oil:		
Oil-wet basis.....	0.1	None
Oil-free basis (approx.).....	0.07	
Cracking temperature.....° F.	780	790
Filtering temperature.....° F.	520	500
Yield of 400° F. E. P. naph. weight per cent.....	9.1	10.4
Yield of gas oil.....do.....	24.2	22.9
Yield of fuel oil bottoms.....do.....	66.7	66.7

Properties of oil	Charge	Fuel oil btms. filtered	Charge	Fuel oil btms.	
				Filtered	Unfiltered
Gravity.....° A. P. I.....		12.7		12.5	
Furol viscosity at 122° F.....		974	3,880	927	615
B. S. & W.....per cent.....	0.1	0.3	0.2	0.2	4.6
Alkalinity					
weight per cent NaOH.....	0.33	0.10	0.41	0.26	0.23
Ash.....weight per cent.....	0.21	0.06	0.20	0.14	0.24
Neutralization No.....	0.06	0.05	0.04	0.02	0.02
Sediment by extraction					
per cent.....	0.02	0.02	0.03	0.07	1.27
Sediment by hot filtration					
per cent.....	0.06	0.09	0.07		2.02
Reduction of alkalinity					
per cent.....		69.7		36.6	43.9
Reduction of ash.....do.....		71.5		30.0	—20.0
Total alkalinity removed					
per cent of original.....		79.8		57.7	62.6
Total ash removed.....do.....		80.9		53.3	20.0

The above data show that cracking alone tends to lower the ash and alkalinity of an oil by a small amount but that this treatment is improved by the use of a small amount of the contact clay. It will also be noted from a comparison of the data in Table V with the data in Table IV that, under cracking conditions, the clay requirements are roughly one-tenth of what they are at 500° F.

The process of this invention may be widely varied and is not to be construed as limited in any manner except as specified in the following claims.

We claim:

1. The method of removing alkali and alkali-containing constituents from a mineral oil containing hydrocarbons capable of yielding low boiling vaporizable reaction products, which comprises the steps of admixing the oil with contact clay which has previously been used in decolorizing and removing acid bodies from acid treated mineral oils, heating the oil-clay mixture to and

maintaining it at a temperature above about 400° F. for a time at least sufficient for the clay to react with and adsorb a substantial portion of the alkali and alkali-containing constituents present in the oil, removing low-boiling vaporizable reaction products from the mixture, and filtering the oil-clay mixture to separate the clay from the oil.

2. Method according to claim 1, in which the temperature is maintained between the limits of about 400° F. and 1000° F.

3. Method according to claim 1, in which the mineral oil is a heavy oil and is maintained at a temperature between about 650° F. and 900° F.

4. Method according to claim 1, in which a reduced crude petroleum is treated.

5. The method of removing alkali and alkali-containing constituents from a heavy crude petroleum residuum oil which comprises the steps of admixing the oil with contact clay which has previously been used in decolorizing and removing acid bodies from acid treated mineral oils, heating the oil-clay mixture to and maintaining it at a temperature above about 400° F. for a time at least sufficient for the clay to react with and adsorb a substantial portion of the alkali and alkali-containing constituents present in the oil, removing low-boiling vaporizable reaction products from the mixture by distillation, and filtering the oil-clay mixture to separate the clay from the oil.

6. Method according to claim 5, in which the temperature is maintained within the range between about 400° F. and 1000° F.

7. The method of cracking a reduced crude petroleum oil and simultaneously removing therefrom alkali and alkali-containing constituents which comprise the steps of admixing the oil with contact clay which has previously been used in decolorizing and removing acid bodies from acid treated mineral oils, heating the oil-clay mixture to and maintaining it at a temperature in the range between about 650° F. and 900° F. for a time sufficient to effect the desired amount of cracking of the oil, removing low-boiling vaporizable reaction products from the oil-clay mixture by distillation, and filtering the oil-clay mixture to separate the clay from the oil.

8. A process as defined in claim 7 wherein said reduced crude petroleum oil is a heavy crude petroleum residuum oil.

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