

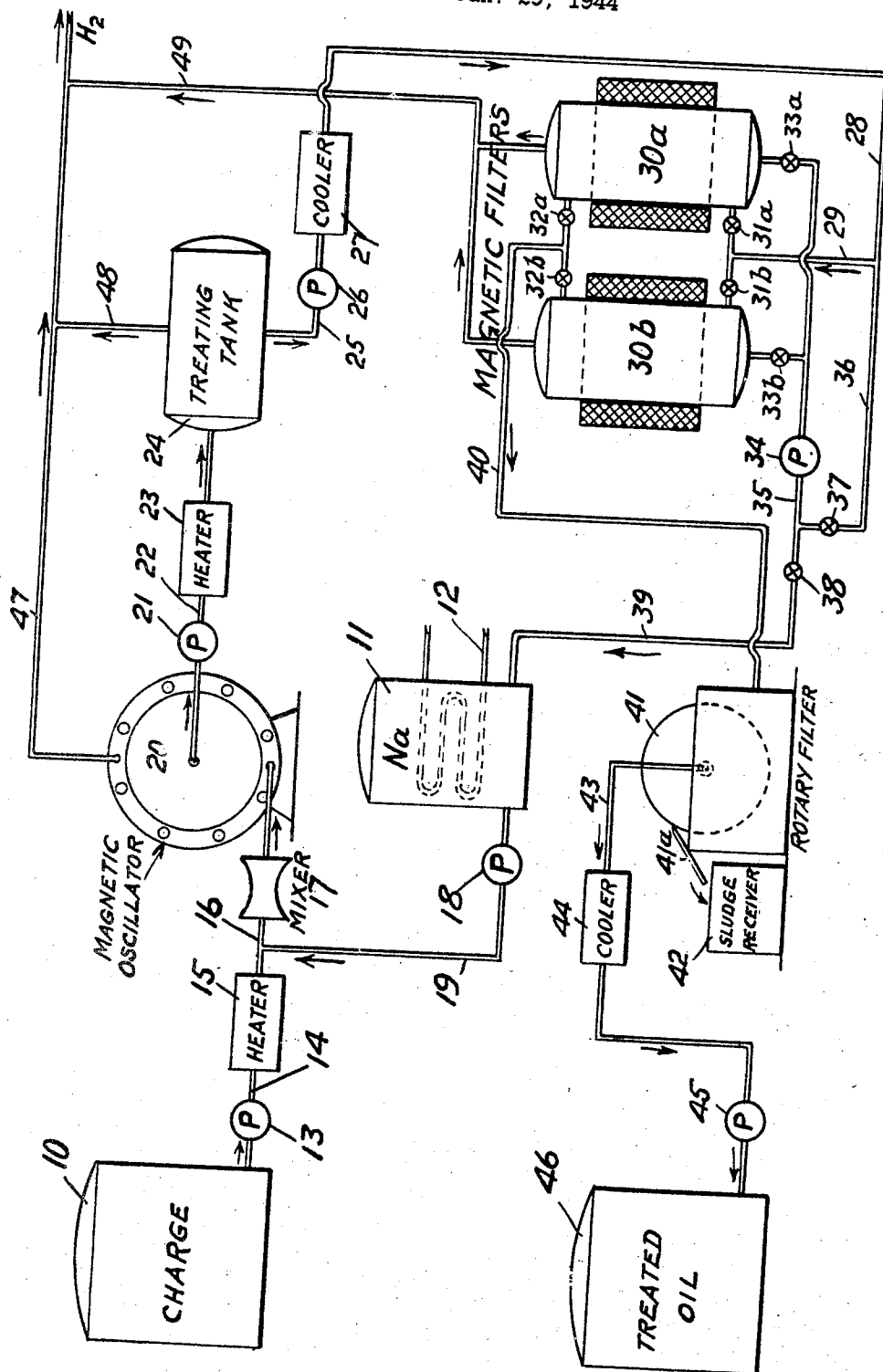
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PROCESS FOR REFINING OF HYDROCARBON OIL WITH METALLIC SODIUM

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PROCESS FOR REFINING OF HYDROCARBON OIL WITH METALLIC SODIUM

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This invention relates to treatment of hydrocarbons with alkali metal and especially to the refining of composite hydrocarbon material, such as the lubricating oil, gas oil, kerosene and gasoline fractions of petroleum, by means of metallic sodium. The invention has particular value in the treatment of lubricating oils for the purpose of improving temperature-viscosity characteristics and other qualities.

The use of metallic sodium as a refining agent in the treatment of petroleum hydrocarbons has long been known and various processes utilizing sodium for this purpose heretofore have been proposed. These, in general, may be classified in two types depending on the relative proportion of sodium used as treating agent. In one type a relatively small proportion of sodium is employed and all or substantially all of the sodium is chemically consumed through reaction with the charge material. Processes of this type have been devised primarily for the purpose of desulfurizing hydrocarbons, especially gasoline. In the other type a relatively large proportion of sodium is used and only a very minor percentage of the treating agent is chemically consumed in the reaction. The excess sodium, representing a preponderant percentage of the total amount employed, acts as a promoter or inductor for reactions in which undesirable constituents of the charge are transformed into reaction products which are readily removable from the more valuable components of the reaction mixture.

The present invention is concerned with this second type of treatment wherein a large excess of sodium is used and may be considered to constitute an improved method of practicing such treatment. An example of a refining process of this type is disclosed and claimed in U. S. Patent No. 1,952,616 issued to me on March 27, 1934. In this process hydrocarbon charge material is treated with a relatively large proportion of sodium—at least 20 parts per 100 parts of charge on a weight basis—at a temperature above the melting point of sodium, with the result that a smaller amount of metal per unit of oil is chemically consumed for a given degree of refining than when a relatively small proportion of sodium is used.

A further example of a process wherein a large excess of sodium is employed as treating agent is given by U. S. Patent No. 2,055,210 issued to me on September 22, 1936. The process described and claimed therein involves the treatment of lubricating oil with a relatively large proportion of sodium in colloidal or quasi-colloidal suspension in the oil. Sodium in such

finely divided form acts as a promoter or inductor, effecting a dehydrogenating reaction wherein charge constituents having less desirable characteristics, particularly the constituents of lower hydrogen to carbon ratio such as aromatic hydrocarbons, are dehydrogenated and transformed into a substantially solid sludge which is readily separable from the more desirable components. The colloiddally dispersed sodium also may cause some hydrogenation of reaction mixture components although it is uncertain as to what extent this occurs. This treatment with colloidal sodium in substantial excess of the amount chemically consumed in the reaction results in a great improvement in properties of the oil, particularly in temperature-viscosity relationship and oxidation stability characteristics. Such results are realizable only when the treating agent is used in substantially colloidal form. In practicing the process described in Patent No. 2,055,210 the proper degree of subdivision of the treating agent is obtained by using a colloid mill to effect mixing of the charge stock and treating agent. The so-formed mixture is maintained at an elevated temperature for a time effective to give the degree of refining desired. This produces a reaction mixture composed of treated hydrocarbons, finely divided sludge and colloiddally dispersed sodium, which is then passed through a filter press to remove sludge and sodium from the treated hydrocarbons. Recovery of the sodium from the filter cake is essential to an economical practice of the process and, as taught in the aforesaid patent, involves the procedure of transferring the filter cake to a ball mill, intimately mixing the filter cake with a liquid agent adapted to coalesce or dissolve the sodium, which agent may be either molten sodium or liquid ammonia, filtering the sodium or solution of sodium from the sludge, and, in the case where ammonia is used, removing the ammonia from the sodium by evaporation. Due to various difficulties in carrying out such a procedure, this method of recovery, although being the best heretofore devised, is not altogether satisfactory for practical operation. Also the use of a colloid mill in effecting the dispersion of sodium in the charge stock likewise has not proved thoroughly satisfactory due to the reactivity of sodium and the tendency of this type of apparatus to admit air into the materials undergoing mixing.

The present invention has particular utility in connection with the above discussed process, although it is not limited thereto in its applicability, and it successfully overcomes the afore-

mentioned difficulties involved in practicing the process. I have now discovered that the excess sodium, present in finely divided form in the reaction mixture, may be separated from the mixture by magnetic attraction and thereby recovered for reuse. Although metallic sodium generally is considered to be non-magnetic, I have discovered that it is sufficiently susceptible to magnetic forces to permit efficient recovery in this manner. Furthermore, I have found that colloidal dispersion of metallic sodium in hydrocarbons may be accomplished in an effective and efficient manner by means of a magnetic oscillator operating on a frequency of vibration at least within the sonic range and permissibly within the range of supersonics.

Thus, in the treatment of hydrocarbons with dispersed metallic sodium in amount substantially in excess of the amount chemically consumed in the reaction, according to the present invention the excess sodium is recovered by means of a magnetic filter or separator. Also, when it is required or desired that the treating agent be employed in very finely divided form, the dispersion preferentially is effected by means of a magnetic oscillator or vibrator. These improvements permit the treatment to be carried out with considerably greater efficiency, economy and simplicity than heretofore possible and are particularly advantageous with regard to safety aspects of handling large-sized quantities of metallic sodium.

The attached flow sheet diagrammatically illustrates a preferred arrangement of apparatus adapted for practicing the invention in a continuous manner. The arrangement, as shown, has particular reference to the treatment of lubricating oil although a similar arrangement would be satisfactory in treating lighter hydrocarbons, for example gasoline, as long as provisions are made for maintaining sufficient pressure to prevent vaporization of the hydrocarbons at the temperature of treatment. Each item of apparatus shown in the flow sheet, including the magnetic oscillator and the magnetic filters, is known and has been used in the arts and therefore need not be illustrated in great detail.

In the drawing 10 designates a storage tank or vessel for the oil to be treated and 11 designates a storage tank for metallic sodium which is maintained in molten condition by means of heating coil 12. The oil is pumped from storage tank 10 by means of pump 13 through line 14 to heater 15 wherein it is heated to a temperature above the melting point of sodium and thence passes through line 16 to mixer 17. Metallic sodium is withdrawn from storage tank 11 by means of pump 18 and passes through line 19 to mixer 17 where it is mixed with the charge oil. Mixer 17 is included in the arrangement merely for the purpose of dispersing the sodium in the oil in moderately fine form so that the mixture passing to magnetic oscillator 20 will be relatively uniform. Mixer 17 suitably may take the form of a Venturi mixer, although other types of mixing equipment, for example a centrifugal pump, also may be used. The mixture of oil and sodium passes from mixer 17 to magnetic oscillator 20. The latter comprises a steel diaphragm which is bolted to a steel cover in a manner to form a chamber therewith and is provided with means (not shown) for vibrating the diaphragm electromagnetically. A frequency of vibration of the diaphragm at least within the sonic range and permissibly in the supersonic range is main-

tained. Within these ranges the frequency is not critical and any desired number of vibrations per second may be utilized. A particularly suitable frequency is 360 vibrations per second since this may be produced conveniently by means of 60 cycle alternating current which has been converted to 180 cycle alternating current by means of a motor generator. As the oil-sodium mixture flows through the chamber of magnetic oscillator 20, the vibration of the diaphragm causes subdivision of the sodium thereby forming a sodium-in-oil dispersion in which the sodium particles are of colloidal or quasi-colloidal size. The resulting mixture flows from the center of magnetic oscillator 20 to booster pump 21 which forces it through line 22 to heater 23 and thence to treating or soaking tank 24. In heater 23 the temperature of the mixture is adjusted to a value within a range above the melting point of sodium but below the cracking temperature of the oil, the particular temperature employed in any given case depending on the charge stock being treated. In the treatment of lubricating oils a temperature of about 400-450° F. generally is preferable, although higher or lower temperatures, for example 350-525° F., also are suitable. In treating tank 24 the mixture is permitted to soak for a time during which the desired reactions take place and until the desired degree of refining is attained. Treating tank 24 should be insulated or provided with heating means in order to maintain the desired reaction temperature.

The reaction mixture from treating tank 23 comprises the refined oil, a solid or substantially solid sludge or polymer in the form of fine particles suspended within the oil, and excess metallic sodium in colloidal form. The mixture is withdrawn through line 25 by means of pump 26 and is pumped through cooler 27 and lines 28 and 29 to filtration apparatus adapted to remove only the sodium, leaving a mixture of oil containing suspended sludge which is separated in a subsequent filtration step. This apparatus consists of one or more magnetic filters or separators illustrated in the drawing as magnetic filters 30-a and 30-b. A preferred type of magnetic filter comprises a chamber or casing enclosing a stack of suitably spaced screens made of magnetic material and a coil or winding surrounding the chamber and suitably energized from an electric power source to effect magnetization of the screens; for example, as illustrated and described in U. S. Patent No. 2,074,085 dated March 16, 1937. Another useful type of magnetic filter in place of screens is illustrated and described in U. S. Patent No. 2,331,769. It, of course, is to be understood that a magnetic filter comprising a permanent magnet to cause magnetization of the screens or vanes instead of an electromagnet also may be used if desired. Preferentially, two or more magnetic filters are employed and are used alternately in order to permit continuous operation. With the arrangement shown in the accompanying drawing, the reaction mixture is caused to flow through magnetic filter 30-a, for example, by opening valves 31-a and 32-a for a time during which the sodium particles are attracted to and retained by the magnetized screens, alternately with which the mixture is made to flow through magnetic filter 30-b by opening valves 31-b and 32-b and closing valves 31-a and 32-a for another period of time. During

the on-stream period of one of the filters, the other filter is drained and the retained sodium is recovered. This is accomplished first by opening either valve 33-a or 33-b as the case may be and, while the off-stream filter is still magnetized, pumping the hydrocarbon mixture out of the filter by means of pump 34 and passing it through line 35 and line 36 containing valve 37 to line 29 wherein it passes along with the reaction mixture coming from treating tank 24 to the on-stream filter. After the filter has been drained of hydrocarbons in this manner, it is demagnetized. The sodium then is withdrawn and pumped by means of pump 34 through line 39 back to storage tank 11 by closing valve 37 and opening valve 38.

In order to effect complete recovery of the sodium particles from the reaction mixture, a magnetic force not less than five times gravity as expressed in the c. g. s. gravitational system of units, should be developed within the magnetic filters. Sodium metal has sufficient magnetic susceptibility so that forces of the aforesaid magnitude imposed upon the colloiddally dispersed sodium particles, will cause complete retention of the particles on the magnetized surface when the reaction mixture is brought into intimate contact therewith. Since the magnetic susceptibility of sodium does not vary substantially over a wide temperature range, the temperature at which the filtration is carried out is not critical. A suitable temperature, for example, is 250° F. but lower or higher temperatures also may be used. It is even permissible to employ a temperature below the melting point of sodium, although this usually is not desirable since it necessitates heating the magnetic filter during the off-stream period in order to melt the retained sodium so that the sodium may be drained from the filter. The operation may be carried out at the same temperature as employed in the treating step and cooler 27 may be eliminated from the system. The cooler is desirable merely as a safety feature in order to permit the steps in the process following the treating step to be carried out at a lower temperature and consequently with less hazard.

The sodium-free mixture of oil and sludge leaves the magnetic filters through line 40 and is sent to equipment for separating the sludge from the refined oil, shown as continuous rotary filter 41. Although this is a preferred form of apparatus for effecting removal of the sludge, other known types of filtration apparatus may be used. Also other methods of separation, for example solvent extraction, distillation or centrifuging, may be used in place of filtration if desired. In the preferred method a layer of sludge or polymer continuously forms on the outer surface of the rotating filter drum and is continuously scraped off by means of knife edge 41a, thence passing to sludge receiver 42. The refined oil is withdrawn from within the filter drum through line 43 and passes through cooler 44 wherein it is cooled to suitable storage temperature. Alternatively, the oil may be cooled to storage temperature prior to the filtration step. From cooler 44 the refined oil is pumped by means of pump 45 to treated oil storage tank 46.

In treating oils with colloidal sodium in relatively large excess of the amount chemically consumed, the sodium acts as a promoter or inductor for reactions in which the charge stock constituents having lower hydrogen to carbon ratio are dehydrogenated and transformed into sludge or polymer, as stated above. Accordingly, the treatment causes the formation of a considerable

proportion of free hydrogen. In treating lubricating oils to the degree of refinement usually desired, roughly 500 cubic feet of hydrogen gas (measured under standard conditions) is liberated per barrel of oil. In the drawing, lines 47, 48 and 49 from magnetic oscillator 28, treating tank 24 and magnetic filters 30-a and 30-b, respectively, are provided to collect the hydrogen evolved. Since the amount of hydrogen formed is considerable, the above-described process may, in one aspect, be considered as a method of manufacturing hydrogen.

In practicing the above-described process the amount of sodium used should be in substantial excess of the amount consumed in the reaction. The amount required to secure the maximum desired degree of refinement of the charge stock material being treated. In treating lubricating oils to effect a high degree of refinement not less than about 16 per cent to 26 per cent sodium by weight of the oil is desirable if not necessary. When such proportions are used, the amount of sodium chemically consumed generally is negligible in comparison to the total amount employed, provided the sulfur content of the charge oil is not excessive.

The following examples illustrate the effect of treating lubricating oils in accordance with the present invention. In these examples three distillate oils derived from naphthenic base crudes were processed substantially as described above and illustrated in the flow sheet with the exception that the sodium-free mixture of defined oil and sludge was cooled to storage temperature before filtering to remove the sludge. Complete recovery of the unreacted sodium from the reaction mixture was attained in the magnetic filtration step. Processing conditions and the characteristics of the oil before and after treatment are shown in the accompanying tabulation.

	Oil I	Oil II
Approximate temperature in magnetic oscillator, ° F.	250	250
Frequency of magnetic oscillator, vibrations/second.	360	360
Temperature of treating, ° F.	425-450	425-450
Time of treating, hours.	11	11
Approximate temperature in magnetic filters, ° F.	250	250
Force developed in magnetic filters.	>5 X gravity	>5 X gravity
Approximate temperature of filtration of Na-free mixture, ° F.	75	75
Lbs. of Na used per bbl. of charge.	70	70
Na consumed in reaction.	Negligible	Negligible
Yield of refined oil, vol. percent of charge.	80	85
Hydrogen formed, cu. ft./bbl. of charge.	480	513

Characteristics of the oil	Before refining	After refining	Before refining	After refining
Gravity, API.	23.5°	27.5°	22.8°	27.0°
Flash point, C. O. C., ° F.	395°	405°	430°	430°
Fire Point, C. O. C., ° F.	465°	455°	515°	490°
Vis. S. U. at 100° F.	218"	178"	490"	325"
Vis. S. U. at 130° F.	102"	93"	211"	161"
Vis. S. U. at 210° F.	44"	44"	57"	53"
Viscosity index.	29	89	55	86
Pour point, ° F.	0°	-5°	-5°	0°
Color, A. S. T. M.	34	2 1/2	3 1/2	2
Demulsibility test.	360	1,560	Poor	1,420
Emulsion test.	Good.	Good.	5 cc.	Good.
Steam emulsion number.	121"	87"		
Neutralization number.	0.03	Neut.	0.08	Neut.
Sulfur, per cent.	0.35	0.08	0.39	0.08
Ash content, per cent.	Trace.	Trace.	Trace.	Trace.
Slight oxidation number.	50.7	0.0	49.8	0.0
Conradson carbon residue.	0.01	0.02	0.02	0.02

Approximate temperature in magnetic oscillator, °F-----	250
Frequency of magnetic oscillator, vibrations/second-----	360
Temperature of treating, °F-----	425-450
Time of treating, hours-----	11
Approximate temperature in magnetic filters, °F-----	250
Force developed in magnetic filters $>5 \times$ gravity	
Approximate temperature of filtration of Na-free mixture, °F-----	75
Lbs. of Na used per bbl. of charge-----	70
Na consumed in reaction-----	Negligible
Yield of refined oil, vol. per cent of charge-----	78
Hydrogen formed, cu. ft./bbl. of charge-----	440

Characteristics of the oil	Before refining	After refining
Gravity, API-----	22.3°	26.8°
Flash point, C. O. C., °F-----	500°	470°
Fire point, C. O. C., °F-----	585°	565°
Vis. S. U. at 100°F-----	1.448"	784"
Vis. S. U. at 130°F-----	507"	325"
Vis. S. U. at 210°F-----	86"	75"
Viscosity index-----	44	90
Pour point, °F-----	0°	0°
Color, A. S. T. M.-----	4½	3½
Demulsibility test-----	900	1,320
Emulsion test-----	Good	Good
Steam emulsion number-----	0.05	Neut.
Neutralization number-----	0.44	0.04
Sulfur, per cent-----	0.44	0.05
Conradson carbon residue-----	Trace	Trace
Ash content, per cent-----	55.9	0.0
Slight oxidation number-----		

The tabulated data show that treatment of naphthenic distillate oils in accordance with the present invention changes their temperature-viscosity relationships to approximate those of paraffin base distillates. By way of comparison, Oil I was solvent extracted by a well known solvent extraction process to yield a product having substantially the same viscosity index as the refined product from Oil I, with the result that a 40 per cent yield of such solvent extracted product was obtained as compared to the 80 per cent yield obtained in the present process. The data also show that the present process causes a marked improvement in oxidation stability of the oil as well as in other characteristics.

I claim:

1. The process of refining liquid hydrocarbon material which comprises subjecting liquid hydrocarbon charge to the action of finely dispersed metallic sodium in amount substantially in excess of the amount chemically consumed in the reaction and at a temperature above the melting point of sodium but below the cracking temperature of the charge, until undesirable constituents of the charge are transformed into a sludge substantially solid at normal temperature, thereby resulting in a reaction mixture comprising refined hydrocarbon material containing sludge and excess sodium in dispersed form, passing said reaction mixture through a separation zone containing a magnetized surface and therein bringing the mixture into contact with said surface and maintaining said surface magnetized sufficiently highly to cause contained sodium particles to be attracted by and retained on said surface, withdrawing the mixture of refined hydrocarbon material and sludge from said separation zone, and then separating refined hydrocarbon material from the sludge.

2. The process defined in claim 1 wherein a magnetic force of intensity not less than five times gravity is magnetically imposed on the sodium particles in said reaction mixture.

3. The process of refining liquid hydrocarbon material which comprises forming a mixture of hydrocarbon charge and metallic sodium in amount substantially in excess of the amount chemically consumed in the reaction, passing said mixture at a temperature above the melting point of sodium but below the cracking temperature of the charge through a magnetic oscillator and therein subjecting the mixture to magnetically induced vibrations of a frequency at least within the sonic range, withdrawing the mixture and passing it to a treating zone, maintaining the mixture within said treating zone at a temperature above the melting point of sodium but below the cracking temperature of the charge until undesirable constituents of the charge are transformed into a sludge substantially solid at normal temperature, thereby resulting in a reaction mixture comprising refined hydrocarbon material containing sludge and excess sodium in dispersed form, passing said reaction mixture through a separation zone containing a magnetized surface and therein bringing the mixture into contact with said surface and maintaining said surface magnetized sufficiently highly to cause contained sodium particles to be attracted by and retained on said surface, withdrawing the mixture of refined hydrocarbon material and sludge from said separation zone and then separating the refined hydrocarbon material from the sludge.

4. The process defined in claim 3 wherein a magnetic force of intensity not less than five times gravity is magnetically imposed on the sodium particles in said reaction mixture.

5. The process defined in claim 3 wherein the frequency of vibration of said magnetic oscillator is approximately 360 vibrations per second.

6. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises subjecting the oil to the action of colloiddally dispersed metallic sodium at a temperature above the melting point of sodium but below the cracking temperature of the oil, until undesirable constituents of the oil are dehydrogenated and rendered a sludge substantially solid at normal temperature, utilizing in said procedure an amount of sodium in excess of that required to effect said dehydrogenation and not less than about 16 per cent to 26 per cent by weight of the oil, thereby resulting in a reaction mixture comprising refined oil containing sludge and excess sodium in dispersed form, passing said reaction mixture through a separation zone containing a magnetized surface and therein bringing the mixture into contact with said surface and maintaining said surface magnetized sufficiently highly to cause contained sodium particles to be attracted by and retained on said surface, withdrawing the mixture of refined oil and sludge from said separation zone and then separating refined oil from the sludge.

7. The process defined in claim 6 wherein a magnetic force of intensity not less than five times gravity is magnetically imposed on the sodium particles in said reaction mixture.

8. The process of improving viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises forming a mixture of the oil and not less than about 16 per cent to 26 per cent metallic sodium by weight of the oil, passing said mixture at a temperature above the melting point of the sodium through a magnetic oscillator and therein subjecting the mixture to magnetically induced vibrations of a

frequency at least within the sonic range to thereby colloidally disperse the sodium in the oil, withdrawing the mixture and passing it to a treating zone, maintaining the mixture within said treating zone at a temperature above the melting point of sodium but below the cracking temperature of the charge until undesirable constituents of the oil are dehydrogenated and transformed into a sludge substantially solid at normal temperature, thereby resulting in a reaction mixture comprising refined oil containing sludge and excess sodium in dispersed form, passing said reaction mixture through a separation zone containing a magnetized surface from which a magnetic force of intensity not less than five times gravity is imposed on the sodium particles in said reaction mixture and therein bringing the mixture into intimate contact with said surface to cause contained sodium particles to be attracted by and retained on said surface, withdrawing the mixture of refined oil and sludge from said separation zone and then separating refined oil from the sludge.

9. The process defined in claim 8 wherein a temperature within the range of 350-525° F. is maintained within said treating zone.

10. The process defined in claim 8 wherein the frequency of vibration of said magnetic oscillator is approximately 360 vibrations per second.

11. The process defined in claim 8 further characterized in that the sodium retained in the magnetic separation zone is separately withdrawn and utilized, together with fresh sodium required to make up for that consumed in the reaction, in the specified treatment of fresh supplies of oil.

12. In a process for refining liquid hydrocarbon material wherein hydrocarbon charge is subjected to the action of finely dispersed metallic sodium in amount substantially in excess of the amount chemically consumed in the reaction and at a temperature above the melting point of sodium but below the cracking temperature of the charge, until undesirable constituents of the charge are transformed into a sludge substantially solid at normal temperature, and the excess sodium is separated from the reaction mixture, the step of separating the excess sodium which comprises bringing the reaction mixture into intimate contact with a magnetized surface from which a magnetic force of intensity not less than five times gravity is imposed on the sodium particles in said reaction mixture to thereby cause the sodium particles to be attracted by and retained on said surface.

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