Sept. 22, 1936. R. S. VOSE 2,055,210

PROCESS OF PRODUCING LUBRICATING OIL

Filed Aug. 21, 1933 3 Sheets-Sheet 1

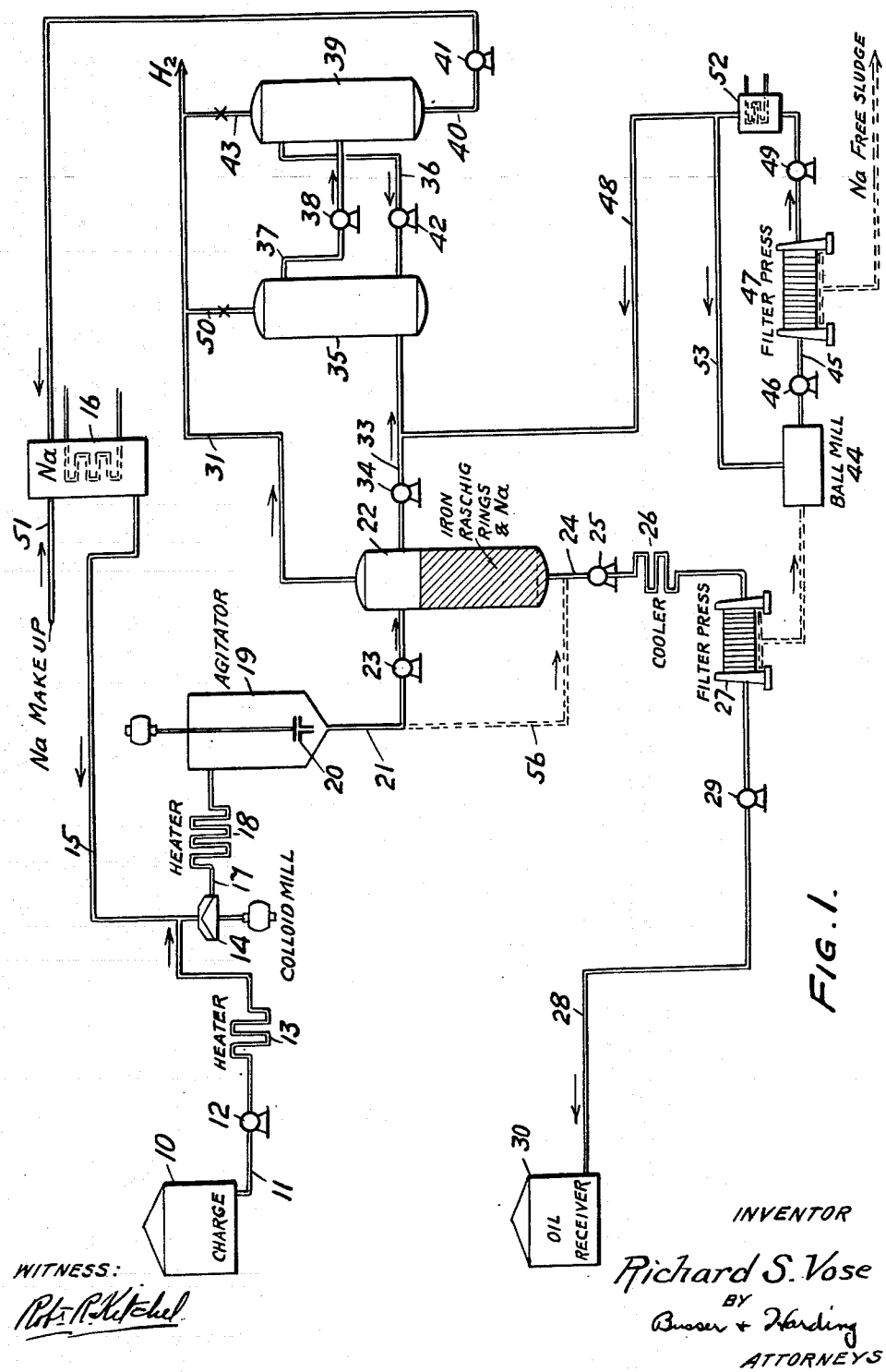


FIG. 1.

WITNESS:
Robt. R. Mitchell

INVENTOR
Richard S. Vose
BY
Busser & Harding
ATTORNEYS.

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PROCESS OF PRODUCING LUBRICATING OIL

Filed Aug. 21, 1933 3 Sheets-Sheet 2

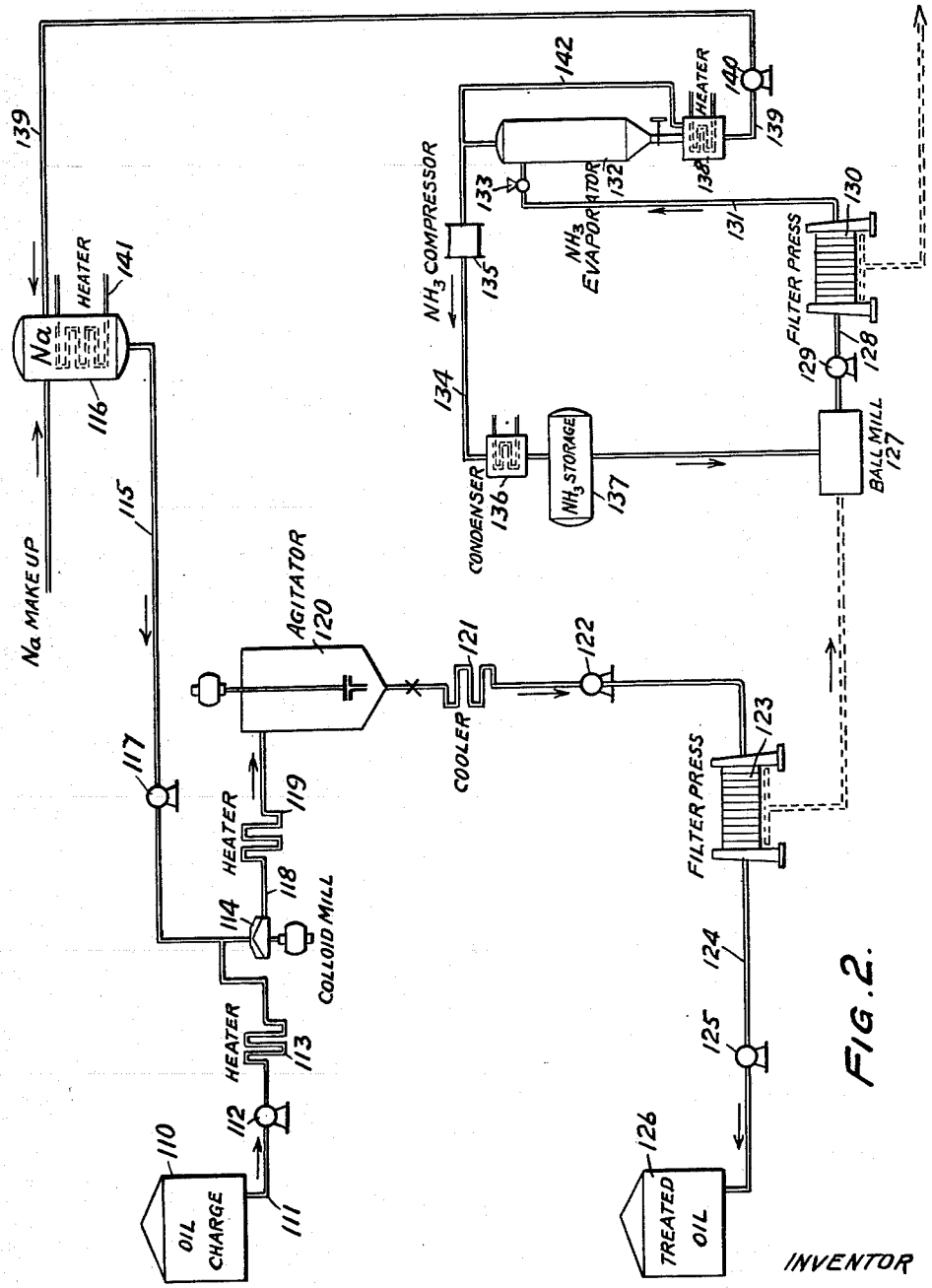


FIG. 2.

INVENTOR

Richard S. Vose

BY

Bisser + Harding

ATTORNEYS.

WITNESS:

Robt. R. Mitchell.

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PROCESS OF PRODUCING LUBRICATING OIL

Filed Aug. 21, 1933 3 Sheets-Sheet 3

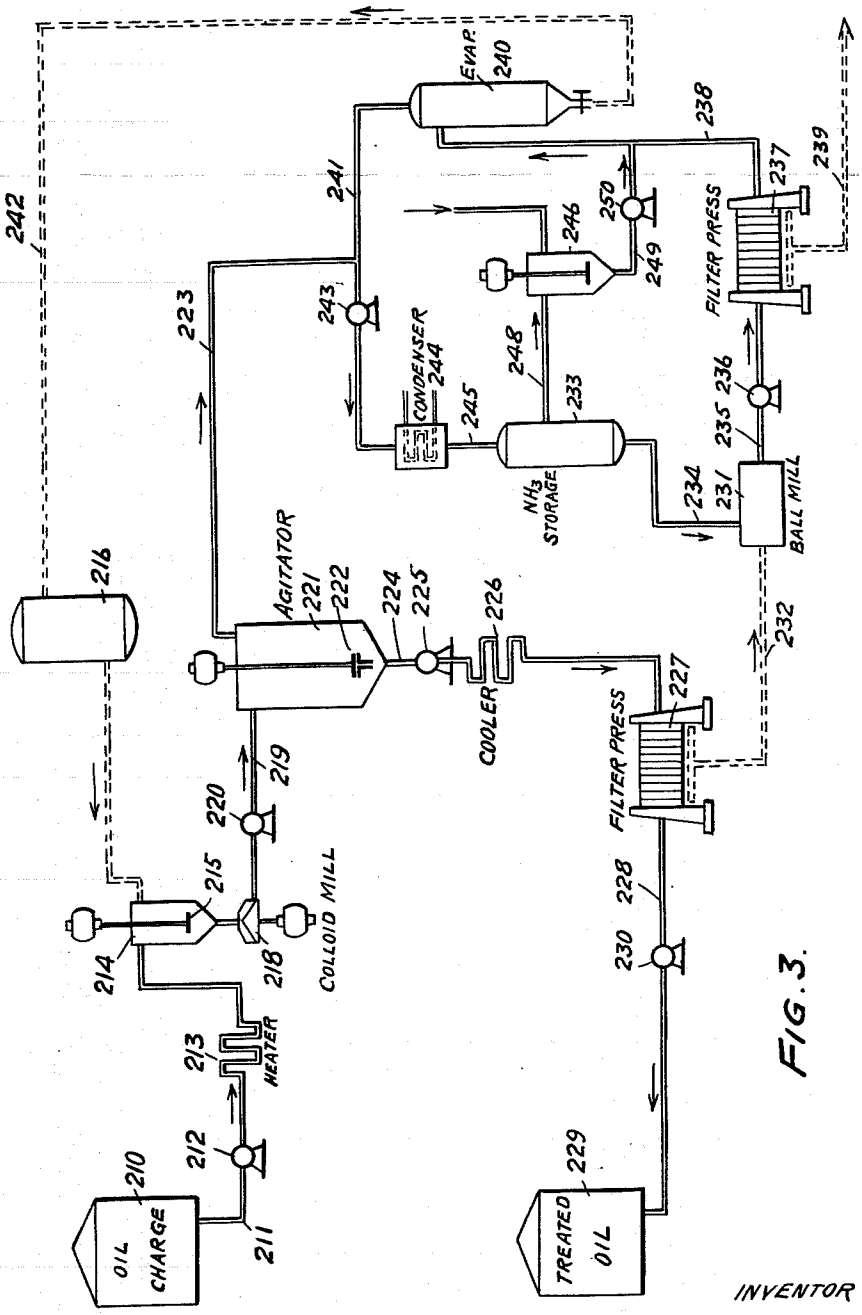


FIG. 3.

INVENTOR

Richard S. Vose

BY

Bussey & Harding

ATTORNEYS.

WITNESS:

Robt. R. Mitchell

Patented Sept. 22, 1936 2,055,210

UNITED STATES PATENT OFFICE

2,055,210

PROCESS OF PRODUCING LUBRICATING OIL

Richard S. Vose, Ridley Park, Pa., assignor to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

Application August 21, 1933, Serial No. 685,994

11 Claims. (Cl. 196—78)

My invention relates to the treatment of lubricating oils with metallic sodium with the object in mind of improving the qualities of the oil. While the process is applicable to the treatment of any lubricating oils, it is particularly applicable to the treatment of naphthenic base lubricating oil distillates for the purpose of effecting a substantial degree of dehydrogenation of the unsaturates, changing their temperature-viscosity characteristics to approximate those of a paraffine base distillate, and substantially improving their qualities in other respects. The process is also applicable to the treatment of petroleum, or petroleum residues, such as mazoot, containing lubricating oil fractions in order to secure, as a product of a subsequent known lubricating oil distillation process, finished lubricating oil distillates having the superior qualities and changed characteristics above briefly mentioned.

The use of metallic sodium for the purpose of improving the qualities of, and particularly for desulphurizing, gasoline is old and well known. The amount of sodium required for such purpose is so small as not to involve a prohibitive expense. But it is impossible to treat lubricating oil with metallic sodium in an amount at all comparable with that required for the treatment of gasoline and secure any substantial improvement in the quality of the oil. It is known, however, to treat naphthenic base lubricating oil with metallic sodium in much greater amounts and substantially improve some of its qualities, but the main objects of my invention, particularly dehydrogenation of unsaturates and change of temperature-viscosity relationship to approximate that characteristic of paraffine base lubricating oils, have not been achieved.

My process for treating lubricating oil distillates, or oil containing lubricating oil fractions before distillation of the lubricating oils, involves the use of a comparatively large amount of metallic sodium at a temperature above its melting point. It requires, also, that the sodium shall form a colloidal or quasi-colloidal suspension in the oil to give a maximum ratio of contact surface to weights of sodium. My invention also involves a process for securing a nearly quantitative recovery of the sodium, without which the process is uneconomical.

Briefly, the present process consists in mixing oil with the proper amount of sodium, at a temperature above the melting point of a sodium, and then passing the oil-sodium mixture through a colloid mill. After passing through the colloid mill, the oil which now contains the sodium in colloidal or quasi-colloidal form is passed through a heater wherein it is heated to the temperature at which it is desired to have the reaction take place. This temperature is usually in the neighborhood of 450° F. Within the reaction chamber the oil-sodium mixture is maintained in a constant state of agitation, the length of time for treatment being varied according to the type of oil being treated, and also according to the purity of the oil being treated. After the oil-sodium mixture has remained in the reaction chamber for a sufficient length of time to insure completion of the reaction, the mixture is drained from the chamber and passed either to a device for coagulating the unreacted sodium which is in colloidal form or through a cooler and then to a filter press for separation of unreacted sodium and sludge produced from the oil. The sludge is then passed to a further stage in the process wherein the unreacted sodium may be removed therefrom, as will hereinafter be more completely described.

The sodium apparently acts as an inductor or promoter for the reaction rather than a catalyst. The reaction is in the nature of a polymerization and/or dehydrogenation of the unsaturated portions of the oil, reducing them to a form in which they may be removed from the oil by filtration or other means. Certain sulphur compounds in the oil, and of course any water present, will react with a very small proportion of the sodium before the sodium begins its role as inductor or promoter. However, this phase of the treatment forms no part of the present invention, as the desulphurization and dehydration of oils by the use of very small amounts of sodium is old, as heretofore set forth. It is generally recognized that the degree of concentration of a catalyst in a reaction mixture does not affect the reaction and that inductors or promoters do affect a reaction mixture by their degree of concentration. Since, therefore, it has been observed that small amounts of sodium do not promote the desired reaction in the oil, it is believed that the conclusion above referred to is correct, namely, that the sodium, after it acts as a direct desulphurization or dehydration reagent, becomes a promoter or inductor for the dehydrogenation reaction.

It is necessary, in order to secure substantial dehydrogenation, that the sodium shall be in colloidal or quasi-colloidal suspension in the oil. It is also admissible, if not necessary, in order to secure the maximum desired dehydrogenation, to use not less than from 170 to 220 grams of sodium per liter of oil, dependent on the oil being treated. It is also necessary to use this mini-

mum proportion of sodium if it be desired to recover anything approaching a quantitative recovery of sodium. As the quantity of sodium is reduced, the proportion possible to recover is reduced. Metallic sodium being comparatively expensive, as compared, for example, with reagents such as sodium hydroxide, its recovery is essential to an economical practice of the process. For the reasons stated, it is desirable, if not necessary, to use a larger proportion of sodium than has heretofore been utilized, as well as to use it in colloidal form.

Alloys such as sodium-potassium, sodium-calcium, sodium-barium, sodium-tin, sodium-lead, and sodium-ammonium may be used in the present process instead of pure sodium. Sodium amalgam may also be used. It is only necessary to carry out the reaction at temperatures above the melting point of the alloy or amalgam, and to reduce the alloy or amalgam to colloidal or quasi-colloidal form. It is of course known that ammonia when in combination with sodium acts as a metal, the combination being, to all intents and purposes, an alloy. Where, in the claims, metallic sodium is specified as the promoting agent, I mean to include, as equivalents, substances such as those above specified, which, when admixed in colloidal condition with oil, act in substantially the same way to effect the same results.

A better understanding of the invention may be had by reference to the accompanying drawings illustrative of different apparatuses for carrying out my process.

Fig. 1 is a diagrammatic flow sheet of apparatus for treating oil with an excess of molten metallic sodium and recovering unused sodium.

Fig. 2 is a diagrammatic flow sheet of an apparatus for treating oil with an excess of molten sodium, and recovering the excess sodium by means of liquid ammonia; and

Fig. 3 is a diagrammatic flow sheet of an apparatus for treating oil with sodium ammonium and recovering the unreacted sodium by means of liquid ammonia.

Referring now to Fig. 1: The numeral 10 designates a storage vessel or tank for the oil to be treated. The oil is removed through line 11, and forced by means of pump 12 through heater 13 to colloid mill 14. Before entering the colloid mill, there is added, to the oil stream in pipe 11, a predetermined amount of molten sodium from line 15, which is in communication with a molten sodium storage vessel 16. On passing through the colloid mill, the sodium and oil are thoroughly mixed, and the molten sodium is reduced to an extremely finely divided condition.

Leading from the colloid mill 14 is line 17, in which is placed heater 18 for heating the oil-sodium mixture. This line 17 leads to an agitator 19 having therein a motor driven centrifugal agitating member 20. There may be provided three or more agitators such as 19 in order, if desired, to make the process a continuous one. The centrifugal agitating member 20 is rotated at an extremely high speed of the order of 9,000 R. P. M. The agitating member itself consists of a disc having a number of radial passages therethrough, and a downwardly extending portion having a passage therethrough which communicates with the radial passages in the disc. By rotating the agitating member at high speeds, the oil-sodium mixture is drawn in through the downwardly extending portion and is expelled through the radial passages by the centrifugal force created by the high rotative speed. The agitator 19 is provided with suitable heating means not shown, to maintain the oil-sodium mixture at reaction temperature during its entire time of treatment. Any suitable heating means may be used, such as electrical resistance heaters or heating coils employing steam or hot oil.

It is practicable, in place of the specific agitator described, to employ agitators of other types commonly used in the treatment of oils. Indeed it may be possible, after the passage through the colloid mill, to dispense with agitation, since agitation is not required to maintain the sodium in suspension in the oil. Agitation, however, is desirable, if not required, to maintain the entire body of oil at a substantially uniform temperature.

From the bottom of the agitator 19 a valved line 21 leads to a tower 22. The treated mixture of oil, sludge and unreacted sodium is forced by means of pump 23 in line 21 into the tower 22. This tower 22 contains packing material 23, which may be iron Rashig or Lessing rings, filling the tower to approximately two-thirds of its capacity.

The oil, containing sludge and some sodium, drains from the bottom of the tower 22, through line 24, containing pump 25, and cooling coils 26, to a filter press 27. There may be provided a number of presses in order that the process may be carried on continuously. Line 28 containing pump 29 leads from a filter press 27 to storage tank 30 for finished oil. The sludge, together with the finely divided sodium, forms filter cakes on the filtering media within the press 27.

Leading from the top of tower 22 is a line 31 for the removal of hydrogen which is formed during the treating step and is adsorbed by the sodium.

From a point below the top of tower 22 there extends a line 33 containing pump 34 for drawing off metallic sodium which is separated in the tower and accumulates to the level of line 33. This metallic sodium is passed to a washing tank 35, wherein it is mixed with naphtha entering through line 36. The mixture of naphtha and sodium is withdrawn from the top of the washing apparatus through line 37 containing pump 38. The naphtha-sodium mixture is thus pumped to a settling chamber 39, wherein the sodium is settled from the naphtha and is pumped out through line 40 by means of pump 41 and returned to sodium storage receptacle 16. The naphtha is removed from near the top of settling tank 39 through line 36 and is returned by means of pump 42 through line 36 to washing apparatus 35.

Lines 50 and 43 lead from the tops of tanks 35 and 39 respectively, to line 31 for the removal of hydrogen which is separated in washing tank 50 and settling tank 39.

The sludge and sodium which accumulate as filter cakes in press 27 are placed in ball mill 44, or in some other suitable grinding apparatus, and therein admixed with molten sodium admitted through line 53. After being thoroughly ground with molten sodium, the mixture is passed through line 45 by means of pump 46, and is forced through filter press 47. The filtering media in press 47 is of a type which will be wetted by metallic sodium and will therefore permit the free coalesced metallic sodium to pass through, but will hold back the sludge, which collects on such filtering medium as a filter cake. The so-

dium which has passed through the press 47 is removed through line 48 and part of it is forced, by means of pump 49, to the sodium washing chamber 35, and the remaining portion is recycled through line 53 to the ball mill 44 for admixture with sodium-containing sludge removed from press 27. When a filter cake of the desired depth has been formed on the media in press 47, it is removed therefrom.

In operation, the oil removed from tank 10, containing the charging stock, is heated in heater 13 to a temperature somewhat above the melting point of metallic sodium (207° F.), and is then passed through line 15 leading to the colloid mill. Line 15, as heretofore explained, conveys molten metallic sodium from the storage receptacle 16 to the colloid mill. The sodium and oil are so proportioned that the charge entering colloid mill 14 is 70 pounds of sodium to 1 barrel of oil (equivalent to approximately 200 grams of sodium to 1 liter of oil). In passing through the colloid mill the sodium is reduced to an extremely finely divided state and thoroughly admixed with the oil. The oil-sodium mixture leaving the colloid mill is then passed through heater 18 wherein it is heated to a temperature within the range of 400°–450° F. Enough oil-sodium mixture is fed to the agitator 19 to fill it to approximately two-thirds of its total capacity. Due to the high rotative speed of the agitating member 20, the oil-sodium mixture is maintained in a state of agitation insuring equal temperature conditions throughout the whole mixture. The oil-sodium mixture is maintained in the highly agitated condition for a period of time ranging from half an hour to thirty-six hours, depending upon the type of oil being treated and the resistance to oxidation or change in temperature-viscosity relationship desired.

Exactly what chemical change takes place in the oil is not known, as the sludge which is recovered has so far resisted all attempts at analysis. However, it has been determined that both dehydrogenation and probably hydrogenation are effected by the sodium treatment. That dehydrogenation is effected is shown by the presence of adsorbed hydrogen in the unreacted sodium. That hydrogenation is effected may be inferred by the change in temperature-viscosity characteristics and the change in specific gravity. The presence of free hydrogen in an adsorbed condition in the unreacted sodium present in the sludge was first detected when analyzing the sludge to determine the amount of sodium which had been reacted. This analysis was carried out by adding alcohol to a weighed sample and determining the amount of hydrogen evolved. Since the amounts of hydrogen evolved were greater than the equivalent of the amount of sodium which was known to be present, it was apparent that free hydrogen must be present. This was also conclusively demonstrated when the sludge was later treated with a further excess of molten sodium, and then washed with naphtha. Since no chemical change was apparent in the naphtha or in the sodium, and since free hydrogen was evolved, there can be no doubt that a dehydrogenation of the original oil took place in the agitator. Since the temperature-viscosity characteristics and the gravity of the oil were also changed, it was evident that dehydrogenation and possibly hydrogenation of the orignal oil had been effected. It is well known that naphthenic base oils have a temperature-viscosity slope differing from the temperature-viscosity slope of paraffin base oils, and when the temperature-viscosity slopes of the untreated and the treated oils were compared, it was found that the treated oil more nearly approximated the temperature-viscosity slope of a paraffin base oil. This fact, coupled with the change in specific gravity, corresponding to increase in the percentage of hydrogen in the oil, leaves no doubt as to the occurrence of dehydrogenation and possibly hydrogenation. It is, of course, evident that if unsaturated components of the original oil are dehydrogenated by the action of the sodium and the dehydrogenated components are removed as sludge, the remaining components of the oil will be substantially saturated. It is also evident that the sodium treatment may dehydrogenate a portion of the unsaturates and hydrogenate the remaining unsaturates. There is concrete evidence of the dehydrogenation and removal of unsaturates but no irrefutable evidence of hydrogenation of a portion of the unsaturates.

The treated oil, containing unreacted sodium and sludge, is drained from the agitator 19 and pumped into the top of packed tower 23, which contains, in addition to the packing, fresh molten sodium. The entering mixture may be considered as an oil-sodium emulsion with the oil in the external continuous phase. Obviously, with such an emulsion, the coalescence of the sodium particles is impossible until the phase is changed and the sodium becomes the external continuous phase, or interlacing phase. This change is accomplished by flowing the oil, sludge and sodium mixture downwardly through the tower 22 which contains Raschig or Lessing ring packing and metallic sodium. In flowing down through the tower, the oil sodium emulsion changes phase and the sodium in the emulsion becomes the external phase, due to the action of the large bath of sodium in the tower, which coalesces the finely divided sodium that mixes with the sodium constituting the bath. In practice, all but about 17 or 18 per cent of the unreacted sodium will be recovered in the tower 22. When refining some light oils, the oil-sodium mixture may have a specific gravity less than that of the molten sodium at the temperature existant in tower 22. In such case the oil-sludge mixture would be admitted to the bottom of tower 22 and flowed upwardly through the sodium. The sodium free oil-sludge mixture would then be withdrawn from tower 22 near the top thereof and the excess sodium at a point below that at which the oil sludge mixture is withdrawn.

The oil-sludge mixture, still containing a small proportion of unreacted sodium, is passed from the bottom of the tower through cooling coils 26 to the filter press 27. Due to the coalescence in the tower of the finely divided sodium present in the oil-sludge mixture, the amount of free sodium in the tower is increased, the excess being drawn off through line 33 and passed to the washing chamber 35.

In some cases it may be desired to eliminate the sodium recovery step in tower 22, in which case the oil-sodium mixture from agitator 19 will be passed directly to pump 25, cooler 26, and press 27 by by-pass 56 shown in dotted lines.

As hereinbefore explained, the oil sludge mixture after being cooled in coils 26 to a temperature approximating 70° F., is passed through the filter press 27, wherein the oil is separated entirely from sludge and unreacted sodium and is passed out through line 28 to storage tank 30.

From time to time the filtering media in press 27 are removed and the sludge cakes accumulated thereon are placed in ball mill 44, and ground with molten metallic sodium. When this grinding is complete, the sludge-sodium mixture is subjected to further pressing in filter press 47. This operation results in the removal of all unreacted sodium from the sludge. The free sodium is then partly recycled to the grinding operation in mill 44, and partly pumped to washing tank 35.

The washing and settling operations remove from the sodium the hydrogen which has been adsorbed therein. In the washing step, carried out in tank 35, a small amount of hydrogen may be released, which is from time to time vented through line 56 to line 31. The naphtha used for washing the sodium to remove adsorbed hydrogen is circulated continuously through the tanks 35 to 39, and is unchanged by the operations performed therein. The sodium is removed from settling tank 39 and is pumped to sodium storage tank 16. Sodium, to make up for that lost in the reaction, is added to storage tank 16 and may be added in the molten state through line 51.

It is to be understood that any low boiling metal may be used to dissolve the unreacted colloidal sodium, or mercury may be used to form a sodium amalgam which can be readily removed from the treated oil or sludge. Such metals as potassium, calcium, barium, tin and lead may be used to coalesce the colloidal sodium and would be equivalent to sodium used for the same purpose.

In all steps from its admission with the oil to the colloid mill to the final removal of all unreacted sodium, except in the step of separating the oil, the sodium is maintained in a molten condition. The temperature in agitator 19 is substantially 450° F. A like temperature prevails in tower 22. Washing apparatus 35 and settling apparatus 39 are also maintained at temperatures above the melting point of sodium. The sodium which is separated with the sludge in filter press 27 has been cooled to a point below its melting point, but is subsequently heated by the addition of molten sodium to ball mill 44. Since the only sodium which circulates through ball mill 44 is that which is recovered, there is provided, preferably in line 48, a heating apparatus 52, to which heat may be supplied, preferably by means of superheated steam circulated through the coil therein, although mineral oil may be used as the heat transmitting medium. Since the melting point of sodium is below the boiling point of water, the handling of molten metallic sodium presents no difficulties whatever. It is, of course, understood that all sodium-carrying lines should be insulated.

The apparatus diagrammatically illustrated in Fig. 2 for the treatment and primary separation of unreacted sodium is substantially the same as that shown in Fig. 1. The method for effecting sodium recovery from the sludge, however, is different in that liquid ammonia is used, necessitating different apparatus. In Fig. 2 the oil to be treated is contained in tank 110 and is removed through line 111 and pumped by means of pump 112 through heater 113 wherein it is heated to a temperature somewhat above the melting point of sodium. The sodium is stored in a molten condition in tank 116, and is fed by means of pump 117 in line 115 to colloid mill 114, together with the heated oil. The oil-sodium mixture then passes through line 118 containing heater 119, in which the mixture is heated to substantially 450° F. The heated mixture is then passed to the agitator 120, which is similar to agitator 19 of Fig. 1. From the agitator 120 the oil and sludge is passed through cooler 121 and therein cooled to approximately 70° F. This mixture is then forced by means of pump 122 through filter press 123. The treated oil emerging from this filter press is passed through line 124 by means of pump 125 to treated oil storage tank 126. The filter cake removed from press 123 is placed in ball mill 127 and is therein agitated with anhydrous liquid ammonia. This mixture is then pumped through line 127 by means of pump 129 to filter press 130. From the filter press 130 is removed what may be said to be a solution of sodium ammonium in liquid ammonia. After filter cakes have been built up in press 130, the filtering media, together with such cakes, which are sodium free, are removed. The sodium ammonium solution removed from the filter press 130 is passed through line 131 to evaporator 132. Placed in line 131 is an expansion valve 133. This permits the expansion and evaporation of the ammonia, and causes the sodium ammonium to be deposited in the bottom of the evaporator in a solid, but more or less finely divided state, the evaporator being maintained at a temperature approximating —27° F. The ammonia in gas form is removed from the top of evaporator 132 by line 134 and is compressed by compressor 135 and passed to condenser 136. This condenser, by removing the heat of compression, restores the ammonia to its liquid form. The liquid ammonia passes from the condenser to an ammonia storage receptacle 137, from which it is drawn for feeding to ball mill 127. It is, of course, understood that ball mill 127 and press 130 must be maintained under sufficient pressure to keep the ammonia in a liquid state.

The sodium ammonium collecting in the bottom of evaporator 132 is removed from time to time to a heater 138, to which heat may be supplied by superheated steam coils. Within the heater 138 the remaining ammonia is driven off and the sodium is restored to its elemental state. The sodium is melted and flows out through line 139 and is passed by pump 140 to sodium storage receptacle 116. The ammonia liberated in heater 138 is passed, by lines 142 and 134 to the compressor and condenser 135 and 136.

Sodium storage receptacle 116 may also be provided with steam coils 141 or other heating means for maintaining the sodium in a molten condition.

Evaporator 132 is shown combined with heater 138, the evaporator having a funnel shaped bottom portion, having a valve or valves therein for permitting the collected sodium to pass from time to time into heater 138. This, however, is not necessary, as the sodium ammonium may be removed and transported to a heater separate from the evaporator.

The apparatus diagrammatically illustrated in Fig. 3 is for the treatment of oil with sodium ammonium instead of with metallic sodium alone, and for the subsequent recovery of unreacted sodium from the sludge. 210 designates an oil supply tank from which oil is drawn for processing. The oil is withdrawn from the tank through line 211 by means of pump 212 and is passed through heater 213 wherein it is heated to a temperature approximating 450° F. From the heater 213 the oil is passed to a mixing chamber 214 having therein a motor driven stirring device 215. As

the oil is admitted to mixer 214, sodium ammonium in granular form is also admitted from a storage receptacle for sodium ammonium, designated in the drawings as 216. Due to the granular state of the sodium ammonium, it cannot be pumped through a pipe line, but must be transferred to the mixing chamber by mechanical means, such as a screw conveyer. This is diagrammatically illustrated in the drawings by dotted line 217. When the sodium ammonium and oil are thoroughly mixed, they are passed to a colloid mill 218, wherein the sodium ammonium is reduced to particles of colloidal size in intimate admixture with the oil. The mixture thus produced is passed through line 219 by means of pump 220 to a reaction chamber 221. This agitator or reaction chamber contains a centrifugal stirring device 222 for maintaining the oil-sodium ammonium mixture in constant agitation and complete admixture.

Due to the effect of heat, a vapor pressure of ammonia will be generated in the agitating chamber 221, and the ammonia released from the mixture as gas will be drawn off through line 223 to compressing and condensing means, to be described hereinafter. The vapor pressure generated within the agitating chamber will by no means approach the vapor pressure of ammonia at treating temperature (450° F.), as the alloying of sodium with ammonia greatly changes the properties of the two components, lowering the tendency to generate high vapor pressures by the application of heat.

After the reaction is completed between the oil and sodium, the mixture is passed by means of line 224 and pump 225 through a cooling coil 226, to a filter press 227 of any desired type. From the filter press the purified and filtered oil is passed to the storage receptacle 229 through line 228, by means of pump 230.

From time to time the sludge containing unreacted sodium and some sodium ammonium is removed in filter cakes from the filter media in press 227 and is transported to a grinding device, which may be a ball mill, designated in the drawings by numeral 231. Since the sludge is not in liquid form, it must be mechanically transported, such as by a screw conveyor, which is illustrated diagrammatically by dotted line 232.

In the grinding device 231 the sludge is thoroughly admixed with liquid ammonia fed through line 234 from a liquid ammonia storage vessel 233. When the admixture of sludge and liquid ammonia is complete and the sodium and sodium ammonium contained in the sludge are thoroughly dissolved in the ammonia, which is added in excess, the solution is forced through line 235 by means of pump 236 into a filter press 237. This filter press serves to hold back the sludge alone, and to permit the solution of sodium ammonium to pass out in a pure state to line 238. The sludge is removed from time to time from the filtering media in the filter press and is transported by mechanical means diagrammatically illustrated by dotted line 239 to a place of disposal.

The sodium ammonium solution leaving press 237 is conveyed by line 238 to an evaporator 240 wherein the excess liquid ammonia is evaporated and passed off through line 241. This evaporating operation leaves the sodium ammonium in a granular state within the bottom of the evaporator. From time to time this granular sodium ammonium is withdrawn and mechanically transported to the storage receptacle 216 by a screw conveyor or other means, which is diagrammatically illustrated by dotted line 242.

The gaseous ammonia withdrawn from agitating vessel 221 and from evaporator 240 is compressed by means of compressor 243 and is cooled in condenser 244 to a temperature sufficiently low to liquify it. The liquid ammonia then passes through line 245 to storage receptacle 233.

It is apparent that the small proportion of sodium which is consumed by the reaction with various products in the oil must be replaced by fresh sodium. This is accomplished by passing sodium to a mixing device 246 through line 247, or merely by dumping lump sodium into the mixing device 246. At the same time, liquid ammonia is withdrawn from storage tank 233 and admitted by line 248 to mixing device 247. When the sodium is completely dissolved in the liquid ammonia, the solution is drawn off through line 249 and pumped by means of pump 250 through line 238 to evaporator 240. In the evaporator the excess liquid ammonia is evaporated in the same manner that the excess liquid ammonia is evaporated from the solution leaving filter press 237. The granular sodium ammonium is then transported to storage receptacle 216.

In carrying out the treatment of oil with sodium ammonium, a certain proportion of sodamide will be formed. This, however, does not disrupt the process, as the action of sodamide on oil is substantially the same as that of sodium ammonium, or metallic sodium itself. It is, however, preferable to remove the sodamide from the process from time to time. This formation of sodamide does not cause any monetary loss, as there is always a market for the same.

The amount of sodium ammonium which must be added to the oil should, of course, be greater than the usual 70 pounds per barrel of oil treated, as the weight of ammonia must be taken into consideration, so that there is always present at least 70 pounds of sodium per barrel of oil treated. As already stated, the temperature of treatment is 450° F. The oil sludge mixture after treatment is cooled to 75° F. in cooler 226 and is then filtered. The sludge is then ground with liquid ammonia in the diagrammatically illustrated grinding apparatus 231, at a temperature of —27° F. At this temperature there is a vapor pressure of only one pound gauge so that the operation may be carried out without the necessity of using expensive pressure equipment. The solution of sodium ammonium containing sludge is then passed through filter press 237 at the temperature of —27° F., and the pure solution which has been freed of sludge is passed to evaporator 240. This evaporator is maintained at any pressure desired, the controlling factor being the rate of evaporation desired, and therefore the temperature at which it is desired to evaporate the excess liquid ammonia. It is, of course, understood that the evaporator 240 must be built to stand the vapor pressure of ammonia at the temperature at which the evaporation is to be carried out.

The treatment of oil with pure metallic sodium is preferred to the treatment of oil with sodium ammonium; and the steps described with reference to Fig. 1 of the drawings for recovering unreacted metallic sodium from the sludge by the addition of a further excess of metallic sodium to coalesce the finely divided particles, are preferred to the recovery steps including the use of liquid ammonia, described in connection with Figs. 2 and 3.

The operations so far described have all been directed to procedure for treating oil with sodium by a batch process. It is to be understood, however, that any one of the three treating and recovering methods hereinbefore described may be carried out in a continuous manner. For instance, oil and sodium in the proper proportions may be charged to agitator 19, (Fig. 1) and the mixture agitated until a sample of the oil upon withdrawal shows that it has reached the degree of purity or dehydrogenation desired. When the oil has reached such a state, fresh oil-sodium mixture is continuously charged to the agitator 19 at a slow rate and treated oil-sludge mixture is continuously withdrawn from the agitator at the same rate that the untreated oil-sodium mixture is charged. The treated oil-sludge mixture is then continuously passed through the tower 22 to coalesce most of the sodium contained in the sludge, and the largely sodium-free mixture is withdrawn from tower 22 and passed through filter press 27. There will, of course, be provided a number of filter presses such as presses 27 and 47, and also several grinding devices, such as ball mill 44, in order that the final recovery of sodium from sludge may be continuous.

The steps just described will also be applicable to the process as shown in Figs. 2 and 3.

Numerous variations of the present process are possible without departing from the spirit and scope of the present invention. For instance, the oil treated may be a distilled lubricating fraction which has or has not been acid treated or subjected to other refining processes such as SO_2 treatment or contact clay treatment, or the oil treated may be a residual lubricating oil which has or has not been subjected to the usual refining steps. The third modification, and probably the most desirable, is the treatment of a reduced crude by the present process before distilling into the various desired lubricating fractions. If it is desired to treat a reduced crude, the fractions including all or light gas oil and all lighter fractions are removed by overhead distillation in any known manner, and the reduced crude or mazoot is treated as hereinbefore described by the addition of an excess of metallic sodium to the mazoot. The mixture is then subjected to the heating and reclaiming steps herein described. It has been stated that this modification is probably the most desirable, since the treating time is greatly lowered. For instance, with some impure lubricating oil fractions, the time of reaction may be as high as 36 hours, but when treating a mazoot with sodium, the reaction time is cut to one-half an hour.

Where, in the claims, I specify mineral oil lubricating oils, I means to include mineral oil, such as reduced crude (which may or may not contain lighter fractions than lubricating oil fractions) but before distillation into lubricating oil distillates, and also mineral oil which consists wholly of a lubricating oil distillate or distillates.

The following specific examples will serve to better illustrate the present process. The following oils, (A, B, C, and D) are all naphthenic base lubricating oil distillates which have not been chemically treated. They are, however, considerably better than the usual distillates before treatment, as they were produced without cracking. These oils were produced by the process described in Pew Patent 1,761,153, to Arthur E. Pew, Jr., dated June 3, 1930.

	Oil "A"		Oil "B"	
	Before Na treating	After Na treating	Before Na treating	After Na treating
Gravity—A. P. I.	21.1	24.1	19.7	23.2
Flash — Cleveland open Cup—°F.	340	335	400	395
Fire—°F.	380	375	460	455
Viscosity—S. U./100°F.	152	144	533	449
Viscosity—S. U./130°F.	70	79	209	179
Viscosity—S. U./210°F.	39	43	54	54
Color—N. P. A.	1¾	1—	2¼	1—
Pour test—°F.	—35	—35	0	—15
Demulsibility	1260	1620	1620	1620
Emulsibility	Good	Good	Good	Good
Steam emulsion	120	17	140	65
Conradson carbon	0.03	0.02	0.05	0.03
Ash	Trace	Trace	Trace	Trace
Reaction	Neutral	Neutral	Neutral	Neutral
Sligh oxidation	51.8	0.0	45.1	0.0
Sulphur—percent	0.23	0.01	0.24	0.01
Temp. of treatment	410–440°F.		410–440°F.	
Time of treatment	40 hours		40 hours	
Temp. for filtration	250° F.		250° F.	
Yield of refined oil as filtrate	70%		75%	
Yield of refined oil from filter cake	15%		15%	
Total yield of refined oil	85%		90%	
Grams of metallic sodium per liter of oil	200		200	
Pounds of metallic sodium per barrel of oil	70		70	

	Oil "C"
Temp. of treatment—° F.	420–440
Time of treatment—hours	20
Temperature of filtration—° F.	70
Oil used—grams	2940
Reagent used—grams	732
Grams of Na per liter of oil	244
Pounds of Na per barrel of oil	85.4
Yield of refined oil	82.5%
Yield of "polymer"	17.5%

Characteristics of the oil	Before refining	After refining
Gravity—A. P. I.	18.3	22.1
Flash—Cleveland open cup—° F.	450	430
Fire	515	510
Vis. Saybolt Univ. at 100° F.	2390	1354
Vis. Saybolt Univ. at 130° F.	672	461
Vis. Saybolt Univ. at 210° F.	88	82
Color—N. P. A.	3¾	1½
Pour test—A. S. T. M.—° F.	+10	0
Demulsibility	300	1620
Emulsibility	Good	Good
Conradson carbon—percent	0.22	0.06
Ash	Trace	Trace
Reaction	Neutral	Neutral
Sligh oxidation	48.1	0.0
Sulphur—percent	0.35	0.02

	Oil "D"
Temp. of treatment—°F.	430–440
Time of treatment—Hours	20
Temp. of filtration—°F.	70
Oil used	3100 grams (3280 cc.)
Reagent used	700 grams
Grams of Na per liter of oil	213
Pounds of Na per barrel of oil	74.6
Yield of refined oil	75.7%
Yield of polymer (by difference)	24.3%

Characteristics of the oil	Before refining	After refining
Gravity—A. P. I.	18.5	23.2
Flash—Cleveland open cup	520	500
Fire	605	585
Vis. S. U. at 100°F.	6113	2219
Vis. S. U. at 130° F.	1515	745
Vis. S. U. at 210° F.	152	109
Color—N. P. A.	—5¾	—1¾
Pour test—A. S. T. M.	+25° F.	+5° F.
Demulsibility	180	1620
Emulsibility	2 cc. Cuff.	Good
Conradson carbon	0.89%	0.12%
Ash	Trace	Trace
Reaction	Neutral	Neutral
Sligh oxidation	65.6	0.0
Sulphur	0.45%	0.03%

The following example will serve to show the results obtained when a mazoot or topped crude, which has been freed of gas oil and all lighter fractions, is treated by the present process.

Oil "E"

Na-Mazoot ratio—grams per liter	200
Na-Mazoot ratio—pounds per barrel	70
Temperature of treatment—°F	450
Time of treatment—hours	1
Agitation	Centrifugal
Temperature of filtration °F	70
Yield of Na—treated mazoot from original mazoot	65
Vac. distillation for lube. oil—mm	2
Yield of zero sligh oxidation lube. oil from treated mazoot—per cent	100
Yield of zero sligh oxidation lube. oil from original mazoot—per cent	65
Yield of zero sligh oxidation tube. oil from crude	47
Per cent Na consumed	1.5
Na consumed per barrel of original mazoot—pounds per barrel	1.1
Na consumed per barrel of treated mazoot—pounds per barrel	1½
Na consumed per barrel of zero sligh oxidation lube. oil obtained—pounds per barrel	1½
Untreated mazoot required per barrel of lube. oil obtained—gallons	65

The mazoot so treated was then subjected to a vacuum distillation to separate the various lubricating fractions.

Analysis by vacuum distillation

Mazoot represents 72.35% of a representative mixture of Gulf Coastal type crudes.

Gravity	19.0
Flash	285° F.
Fire	330° F.
Viscosity at 100° F	1047
Viscosity at 210° F	74
Pour test	—10° F.
Sulphur	0.46%
Charge	1400 cc.
Gravity	23.7
Neutral number	Neutral
Conradson carbon	0.19
Ash—per cent	Trace
Sulphur—per cent	0.09

The following example will show the treatment of oil with sodium ammonium:

	Oil "F"
Quantity	3600 cc.
$NaNH_2$	1160 grams
Ratio Na/oil	
Grams per liter	185
Pounds per barrel	65
Ratio $NaNH_2$/oil	
Grams per liter	322
Pounds per barrel	113
Temp. of treatment	425–450° F.
Time of treatment	8½ hours
Agitation	Centrifugal
Temp. of filtration	75° F.

Characteristics of the oil	Original	Treated
Gravity A. P. I.	18.3	20.8
Flash ° F	450	435
Fire ° F	515	510
Viscosity at 100° F	2390	1654
Viscosity at 130° F	672	520
Viscosity at 210° F	88	82
Pour test ° F	+10	0
Color	3¾	5
Conradson carbon	0.22	0.12
Ash	Trace	Trace
Sligh oxidation	48.1	8.7
Sulphur percent	0.35	0.02

After separating the oil from the sludge by filtration, the sludge was ground with liquid ammonia and subsequently filtered to separate the ammonia-sodium solution from the sludge, and the excess ammonia then evaporated from the solution. This resulted in 100% recovery of unreacted sodium from the sludge.

Oil "G"

Initial charge (200 gr./liter)	678 grams sodium
Temp. of treatment	425–450° F.
Time of initial treatment	13¼ hours
Rate of continuous treatment	
Oil	4.5 cc./minute
Na	1.0 grams/minute
Efflux	5.2 grams/minute
Consumption of Na during treatment	No appreciable amount
Recovery of sodium	
1st step	82.1% of total sodium
2nd step	68.5% of remainder
Overall recovery	94.4%

	Temp.		mm. pres.	Percent chg.	A. P. I. grav.	°F. flash	°F. fire	Vis.—°F.			Sligh oxid.	Color N.P.A.	S. E.	Percent sulphur	Neut. No.	Con. carbon
	Vap.	Liq.						100	130	210						
Init.		305	2													
5%	296	345	2													
Cut 1	332	377	2	10	28.4	225	250	41	36		0.0	1—	16		Neut.	0.02
2	370	415	2	10	26.4	275	305	56	36		0.0	1—	31	0.01	Neut.	0.01
3	404	450	2	10	25.2	310	355	90	58		0.0	1—	30		Neut.	0.02
4	428	470	2	10	24.0	345	410	214		43	0.0	1—	41		Neut.	0.02
5	475	510	2	10	23.2	385	450	372		49	0.0	1+	91	0.01	Neut.	0.01
6	498	542	2	10	22.4	420	490	863		63	0.0	1½			Neut.	0.02
7	535	590	2	10	21.9	460	535	1,537		81	0.0	1½+			Neut.	0.04
8	600	670	2	10	22.7	505	570		754	104	0.0	2+		0.05	Neut.	0.08
9	668	775	1½	10	23.1	505	625		1,150	153	0.0	3+			Neut.	0.20
Btms.				10	21.7	635	730		5,560	480	0.0	Dk.red		0.09	Neut.	1.15
Total				100												
Tops				90												
Btms.				10												

Bottoms {Ash—trace / Sulphur—0.07}

Temp. of recovery
1st step..... 450° F.
2nd step..... 250° F.

Yield of refined oil
Average..... 80%

Sodium used for refining.. 70 pounds per barrel

A mixture of oil and sodium was treated in an agitator such as shown in Fig. 1 of the drawings, at 450° F., the ratio of oil sodium being 200 gr. Na per liter of oil (70 pounds sodium per barrel of oil), until a sample of the oil, on being withdrawn and filtered, showed a zero sligh oxidation number. When oil having zero sligh oxidation characteristics was obtained, a continuous stream of untreated oil admixed with sodium in the same ratio as before stated was supplied to the agitator, and at the same time continuous removal of treated oil was effected at the same rate the untreated oil and sodium were added. This efflux of treated oil was run directly and continuously into a sodium recovery tower, such as shown (22) in Fig. 1 of the drawings, which was packed with iron Lessing rings and charged with fresh sodium. The charge of fresh molten sodium in the tower caused the coalescence of a portion of the unreacted sodium present in the sludge. The efflux from the bottom of the tower was continuously cooled and passed through a filter press having canvas filtering media to separate the refined oil from sludge and the remaining excess sodium. The pressed dry filter cake was then run into a mechanical mixer, in which it was ground with fresh molted sodium at a temperature of 250° F. After sufficient contact in the grinding mill, the mixture was filtered through canvas and the filter cake was pressed in a hydraulic press to remove the excess sodium.

In the foregoing specific examples the sodium-oil ratios have been given in pounds per gallon or grams per liter. The following table shows the sodium-oil ratios on the basis of weight alone for the first six specific examples:

	A. P. I. gravity	Density	Gr. Na per liter oil	Percent Na by weight	Oil/Na ratio
				Percent	
Oil A	21.1	.927	200	21.5	4.62/1
Oil B	19.7	.936	200	21.3	4.68/1
Oil C	18.3	.945	244	25.8	3.87/1
Oil D	18.5	.943	213	22.5	4.42/1
Oil E	19.0	.940	200	21.2	4.7/1
Oil F	18.3	.945	185	19.5	5.1/1

The gravities of lubricating oils vary between 17° and 35° A. P. I., it is therefore more convenient to express the oil-sodium ratios on the basis of weight alone and for this reason the following data is given to show the range of percentage of sodium possible where the oils are treated with 170 to 220 cc. of sodium per liter of oil:

	Percent Na by weight of oil	
	170 grams per liter	220 grams per liter
	Percent	*Percent*
35 A. P. I. Gravity oil	20	25.9
17 A. P. I. Gravity oil	16.6	23

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

1. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises dehydrogenating unsaturated constituents of the oil by subjecting the oil to the action of colloidally dispersed metallic sodium, in an amount substantially in excess of that required to desulphurize and at a temperature above the melting point of sodium but below the cracking temperature of the oil, until unsaturates are dehydrogenated and rendered a sludge substantially solid at normal temperature and separable from the oil, and removing hydrogen, sludge, and sodium from the oil.

2. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises subjecting the oil to the action of colloidally dispersed metallic sodium, at a temperature above the melting point of sodium but below the cracking temperature of the oil, until unsaturates are dehydrogenated and rendered substantially solid at normal temperature and separable from the oil, utilizing in said procedure an amount of sodium in excess of that required to effect said dehydrogenation and not less than about 16% to 26% by weight of the oil so as to enable it to be subsequently separated, separating the oil from the sodium and dehydrogenated unsaturates and separating the sodium from the dehydrogenated unsaturates.

3. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises subjecting the oil to the action of colloidally dispersed metallic sodium, at a temperature above the melting point of sodium, but below the cracking temperature of the oil, until unsaturates are dehydrogenated and rendered substantially solid at normal temperature and separable from the oil, utilizing in said procedure an amount of sodium in excess of that required to effect said dehydrogenation and not less than about 16% to 26% by weight of the oil so as to enable it to be subsequently separated, separating the oil from the sodium and dehydrogenated unsaturates, separating the sodium from the dehydrogenated unsaturates, treating the sodium with a washing fluid adapted to separate adsorbed hydrogen therefrom, separating the sodium from the said washing fluid and utilizing the separated sodium, together with fresh sodium required to make up for that lost in the reaction, in the above specified treatment of fresh supplies of oil.

4. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises dehydrogenating unsaturated constituents of the oil by subjecting the oil to the action of colloidally dispersed metallic sodium in an amount substantially in excess of that required to desulphurize and at a temperature above the melting point of sodium but below the cracking temperature of the oil, agitating the oil-sodium mixture until unsaturates are dehydrogenated and rendered a sludge substantially solid at normal temperature and separable from the oil, and removing hydrogen, sludge, and sodium from the oil.

5. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises dehydrogenating unsaturated constituents of the oil by subjecting the oil to the action of colloidally dispersed metallic sodium, in an amount substantially in excess of that required to desulphurize and at a temperature above the melting point of

sodium but below the cracking temperature of the oil, until unsaturates are dehydrogenated and rendered a sludge substantially solid at normal temperature and separable from the oil, passing the oil-sodium-sludge mixture into contact with a solvent adapted to coalesce and selectively dissolve colloidal sodium, removing oil and sludge from the coalesced sodium, and then separating treated oil from the sludge.

6. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises dehydrogenating unsaturated constituents of the oil by subjecting the oil to the action of colloidally dispersed metallic sodium, in an amount substantially in excess of that required to desulphurize and at a temperature above the melting point of sodium but below the cracking temperature of the oil, until unsaturates are dehydrogenated and rendered a sludge substantially solid at normal temperature and separable from the oil, passing the oil-sodium-sludge mixture into contact with a solvent adapted to coalesce and selectively dissolve a portion of the colloidal sodium, removing oil and sludge from the coalesced sodium, then separating treated oil from the sludge and removing further sodium from the sludge and utilizing the sodium separated as specified in the above defined treatment of fresh supplies of oil.

7. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises dehydrogenating unsaturated constituents of the oil by subjecting the oil to the action of colloidally dispersed metallic sodium, in an amount substantially in excess of that required to desulphurize and at a temperature above the melting point of sodium but below the cracking temperature of the oil, until unsaturates are dehydrogenated and rendered a sludge substantially solid at normal temperature and separable from the oil, passing the oil-sodium-sludge mixture into contact with a substantially larger amount of molten metallic sodium to coalesce colloidal sodium, removing oil and sludge from the coalesced sodium, and then separating treated oil from the sludge.

8. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises dehydrogenating unsaturated constituents of the oil by subjecting the oil to the action of colloidally dispersed metallic sodium, in an amount substantially in excess of that required to desulphurize and at a temperature above the melting point of sodium but below the cracking temperature of the oil, until unsaturates are dehydrogenated and rendered a sludge substantially solid at normal temperature and separable from the oil, passing the oil-sodium-sludge mixture into contact with a substantially larger amount of molten metallic sodium to coalesce a portion of the colloidal sodium, removing oil and sludge from the coalesced sodium, then separating treated oil from the sludge and removing further sodium from the sludge by grinding it with liquid metallic sodium.

9. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprise dehydrogenating unsaturated constituents of the oil by subjecting the oil to the action of colloidally dispersed metallic sodium, in an amount substantially in excess of that required to desulphurize and at a temperature above the melting point of sodium but below the cracking temperature of the oil, until unsaturates are dehydrogenated and rendered a sludge substantially solid at normal temperature and separable from the oil, passing the oil-sodium-sludge mixture into contact with a substantially larger amount of molten metallic sodium to coalesce a portion of the colloidal sodium, removing oil and sludge from the coalesced sodium, then separating treated oil from the sludge and removing further sodium from the sludge by grinding it with liquid ammonia separating the liquid ammonia from the sodium and utilizing the separated sodium, together with fresh sodium required to make up for that lost in the reaction, in the above specified treatment of fresh supplies of oil.

10. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises dehydrogenating unsaturated constituents of the oil by subjecting the oil to the action of colloidally dispersed metallic sodium, in an amount substantially in excess of that required to desulphurize and at a temperature above the melting point of sodium but below the cracking temperature of the oil, until unsaturates are dehydrogenated and rendered a sludge substantially solid at normal temperature and separable from the oil, removing hydrogen, sludge and sodium from the oil, and dissolving the sodium with sludge in liquid ammonia, then separating from the sludge the sodium ammonium so formed and hydrogen adsorbed by the sodium during the dehydrogenation reaction separating the ammonia and hydrogen from the sodium and utilizing the separated sodium, together with fresh sodium required to make up for that lost in the reaction, in the above specified treatment of fresh supplies of oil.

11. The process of improving the viscosity-temperature characteristics and other qualities of mineral lubricating oils which comprises dehydrogenating unsaturated constituents of the oil by subjecting the oil to the action of colloidally dispersed metallic sodium, in an amount substantially in excess of that required to desulphurize and at a temperature above the melting point of sodium but below the cracking temperature of the oil, until unsaturates are dehydrogenated and rendered a sludge substantially solid at normal temperature and separable from the oil, passing the oil sodium mixture into contact with a solvent adapted to coalesce and selectively dissolve colloidal sodium, removing oil and sludge from the coalesced sodium, and filtering the same to recover treated oil from the sludge.

RICHARD S. VOSE.