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## PROCESS FOR REFINING HYDROCARBON OILS

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10 Claims. (Cl. 196—23)

This invention relates to the treatment of hydrocarbon materials and more particularly to the refining of lubricating oils.

Lubricating oils are commonly refined by treating with sulfuric acid, caustic or other chemicals, and with adsorbent materials such as fuller's earth. It is known that alkali metals are superior to other treating agents for the refining of hydrocarbon oils but their relatively high cost has prohibited their use. The methods heretofore proposed for treating hydrocarbon oils with alkali metal consist in general in agitating the oil with excess molten alkali metal at a suitable temperature and separating refined oil from the resulting mixture of unreacted metal and insoluble treatment by-product or "polymer". After the refined oil has been removed, a pasty mixture of "polymer" and metal remains, from which it is difficult and expensive to recover the metal. This recovery problem is especially difficult in the treatment of the heavier oils.

One object of this invention is to provide a process for treating hydrocarbon oils with an excess of alkali metal, whereby practically complete recovery of unreacted metal is possible. A further object is to provide such a process in which the amount of alkali metal consumed per unit of refined oil is less than that which has been possible heretofore. Other objects will be hereinafter apparent.

These objects are attained by treating oil with a large excess of alkali metal and carrying out the treatment under such conditions that on settling, the unreacted alkali metal remaining after treatment tends to agglomerate into large masses which may be separated from the refined oil and from the "polymer" by simple means.

I have discovered the surprising fact that for a given treating temperature, when a liquid hydrocarbon material is treated with an unusually large excess of alkali metal, a smaller amount of the metal per unit of oil is chemically consumed for a given degree of refining, than when a small excess of metal is used. Furthermore, by use of the large excess of alkali metal, less insoluble polymer is formed, which simplifies the problem of recovering unreacted metal. I have found that if the excess of sodium is of the proper magnitude and if the agitation during treatment is kept to the minimum required to obtain the desired refining effect, at the end of the treatment the unreacted alkali metal may be easily caused to agglomerate into one or several large masses. I have further discovered that such a mass of alkali metal maintained in the liquid state may be filtered through a filter medium which is wet with oil. This discovery makes it possible to filter refined oil and liquid alkali metal in one operation from the insoluble treatment by-products or "polymer".

To refine hydrocarbon oil according to the present invention, the oil is agitated with an amount of alkali metal equal to at least 20% of the weight of the oil at a temperature above the melting point of the metal, for instance at 100° C. or higher. I prefer to use 20–30 pounds of alkali metal for each 100 pounds of oil. In general, the amount of alkali metal reacted per unit of oil during the treatment is an inverse function of the ratio of metal used to oil treated. The temperature is preferably maintained at 175°–250° C. The required time of treatment depends on the amount of alkali metal present per unit of oil, temperature, degree of agitation, nature of the oil and degree of refinement desired. The treating period in general will be from 5 to 48 hours. For a given degree of refinement the time required is an inverse function of the temperature, amount of alkali metal per unit of oil, and degree of agitation.

It is preferable to adjust the degree of agitation so that the particles of alkali metal will be large enough to agglomerate readily when the mixture is allowed to settle. The readiness with which such agglomeration will occur depends not only on the size of the metal globules but also on the amount of polymer formed, since a coating of polymer on the metal tends to prevent agglomeration. The amount of polymer formed is usually an inverse function of the amount of metal present and also is dependent on the nature of the oil. Hence, for each kind of oil, there is a minimum proportion of alkali metal that may be used so that agglomeration may occur readily; and this may be determined by experimenting with small batches. Slow or sluggish agitation is, in general, sufficient to effect good contact without emulsifying the metal. Oils of higher viscosity require the use of a larger excess of metal in order to agglomerate the metal readily at the end of the run. Also, oils which produce relatively large amounts of polymer should be refined with a larger excess of alkali metal.

The treatment of the oil is discontinued when examination of a sample taken from the treating vessel shows that the desired degree of refining has been reached. This may be determined by subjecting the sample to standardized tests for color, etc., or by testing samples, freed of alkali metal and insoluble polymer, for alkalinity. If a filtered sample is substantially neutral to phenolphthalein in alcohol and light colored or water white, the maximum degree of refinement practically possible has been substantially reached.

When a test shows the oil to be sufficiently refined, agitation is stopped and the mixture is allowed to settle; but preferably it is not allowed to cool below the melting point of the alkali metal. The mass is then filtered hot, that is, at a temperature above the melting point of the alkali metal, preferably through a cloth or paper filter. When most of the oil has passed through the filter medium, the unreacted alkali metal begins to pass through, finally leaving a residue of insoluble polymer which may contain a small amount, for instance 3% or less, of alkali metal. The metal appearing in the filtrate readily agglomerates into one mass and may be separated from the refined oil by simple mechanical means, for instance by decantation.

The following examples illustrate my invention by showing the effects of using large amounts of alkali metal in treating hydrocarbon oils.

*Example 1*

Four portions of an acid-refined, asphalt base lubricating oil, having a specific gravity of 0.898 and an S. U. V. viscosity of 150 seconds at 100° F., were treated separately by agitating at about 225° C. with different amounts of sodium but with the same degree of agitation. Each run was continued until a sample, taken from the treating vessel, filtered and tested with a mixture of alcohol and water containing phenolphthalein, no longer gave an alkaline reaction. After each run, the amount of sodium which had reacted was determined. The data for these runs are given in the following table:

| Run | Time of treatment | Sodium used | | Sodium reacted (lbs. per bbl. of oil) |
|---|---|---|---|---|
| | | Lbs. of sodium per bbl. of oil | Percent of sodium by wt. of oil | |
| | *Hours* | | | |
| 1 | 10½ | 26 | 8.3 | 15.4 |
| 2 | 9 | 35 | 11.1 | 14.0 |
| 3 | 4½ | 52 | 16.5 | 14.6 |
| 4 | 3 | 70 | 22.2 | 8.2 |

The degree of refining obtained in each run is indicated by the following data. The characteristics of the oils were determined by the standard methods of the American Society for Testing Materials.

| Characteristic | Untreated oil | Run #1 | Run #2 | Run #3 | Run #4 |
|---|---|---|---|---|---|
| Neutralization No. | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Color (N.P.A.) | No. 2 | Lighter than No. 1 in all runs. | | | |
| Sligh oxidation No. | 14.1 | 1.9 | 0.8 | 1.2 | 0.3 |
| Steam emulsion No. | | 0.0 | 45 sec. | 0 | 0 |

*Example 2*

Two portions of an asphalt base oil having a specific gravity of 0.9047 and a viscosity of 60 seconds S. U. V. at 100° F. were treated at about 175° C. with different amounts of sodium and the same degree of agitation, whereby practically the same degree of refinement was obtained in each case. The amounts of sodium reacted are shown in the following table:

| Run | Time of treatment | Sodium used | | Sodium reacted (lbs. per bbl. of oil) |
|---|---|---|---|---|
| | | Lbs. of sodium per bbl. of oil | Percent of sodium by wt. of oil | |
| | *Hours* | | | |
| 1 | 10½ | 26.5 | 7.9 | 11.2 |
| 2 | 9½ | 70.0 | 24.0 | 8.8 |

The degree of refining obtained was substantially the same in both runs. The refinement obtained in Run No. 2 is shown by the following data:

| Property | Oil before sodium treatment | Sodium-treated oil |
|---|---|---|
| Neutralization No. | 0.00 | 0.00. |
| Color | No. 1½, N. P. A. | Water white. Better than 23 Saybolt. |
| Sligh oxidation No. | 12.6 | 0.3. |
| Steam emulsion No. | 57 secs. | 0. |

From the above example, it is seen that when the proportional amount of alkali metal is increased beyond a certain point, a surprising and unexpected result is obtained, namely that considerably less metal is reacted and the time of operation is shortened, to produce the maximum practical degree of refinement. This point, in Example 1, corresponds to an amount of sodium equal to somewhere between 16.5% and 22.2% of the weight of the oil. In general, this point will vary with different oils, but will usually correspond to at least 20% of the weight of the oil.

It is understood that my invention is not limited to the specific methods of operation described above, but comprises any method of contacting hydrocarbon material in the liquid phase with the proportions of alkali metal herein set forth. The process may be made continuous without departing from the scope of this invention. If desired, the step comprising separation of unreacted alkali metal from the treatment by-products may be omitted. Various other modifications which come within the scope of my invention will be apparent to those skilled in operating similar processes.

I believe that the surprising results obtained by my invention may be explained by assuming that when alkali metal is contacted with a hydrocarbon substance, its refining action is dependent upon (1) a chemical reaction with the oil, and (2) a catalytic action. This catalytic action may or may not be similar to that produced by adsorbent substances such as fuller's earth, but in any event it is many times as powerful as the catalytic action of such adsorbents. When the proportion of alkali metal is increased to beyond a certain point the catalytic action apparently predominates over the chemical action, causing a high degree of refinement of the oil with the occurrence of comparatively little chemical action. Although this appears to be a plausible explanation of the process, I do not wish to limit my invention thereby.

My process may be used to refine any hydrocarbon material in the liquid state and is especially useful for hydrocarbon oils having a viscosity greater than 50 seconds S. U. V. at 100° F. It may be used to produce high grade water white medicinal oils or oils for lubricating purposes where a high degree of chemical stability is essential, for instance, steam turbine oils and transformer oils.

An important advantage of my invention over previous methods of alkali metal treatment is that less alkali metal and oil react, resulting in the formation of less polymer, a better yield of refined oil and a smaller consumption of alkali metal. A further advantage is that it provides a means for easily recovering substantially all of the unreacted alkali metal remaining after the treatment of an oil. My process is also superior to other methods of treating oils such as acid, caustic or adsorbent treatments because it will produce in one operation a degree of refining which may be obtained by these other processes only by a multiplicity of treatments. Furthermore, my process produces a refined oil of as good or better quality than that obtainable by prior methods and with a higher yield. In some cases my process has a further advantage in that by its use the time required to obtain a given degree of refining by alkali metal treatment may be considerably shortened.

I claim:

1. A process for refining liquid hydrocarbon material comprising agitating said material with an amount of alkali metal equal to not less than 20% by weight of said oil at a temperature above the melting point of said metal, and filtering to separate the reaction by-products from the refined oil and unreacted molten metal.

2. A process for refining hydrocarbon oil comprising agitating said oil with an amount of alkali metal equal to not less than 20% by weight of the oil at a temperature of 100–250° C., and filtering to separate the reaction by-products from the refined oil and unreacted molten alkali metal.

3. A process for refining hydrocarbon oil comprising agitating said oil with an amount of sodium equal to 20–30% by weight of the oil at a temperature of 100–250° C., and filtering to separate the reaction by-products from the refined oil and unreacted molten sodium.

4. A process for refining hydrocarbon oil comprising agitating said oil with an amount of sodium equal to 20–30% by weight of the oil at a temperature of about 225° C. for 5–48 hours, and filtering to separate the reaction by-products from the refined oil and unreacted molten sodium.

5. A process for refining hydrocarbon oil comprising agitating said oil with an amount of alkali metal equal to 20–30% by weight of the oil at a temperature of 100–250° C., allowing the mixture to settle, hot filtering to remove insoluble treatment by-products and separating refined oil from residual alkali metal.

6. A process for refining hydrocarbon oil comprising agitating said oil with an amount of sodium equal to 20–30% by weight of the oil at a temperature of 100–250° C., allowing the mixture to settle, hot filtering to remove insoluble treatment by-products and separating refined oil from unreacted sodium.

7. A process for refining hydrocarbon oil comprising agitating said oil with an amount of sodium equal to 20–30% by weight of the oil at a temperature of about 225° C. for 5–48 hours, allowing the mixture to settle, hot filtering to remove insoluble treatment by-products and separating refined oil from residual sodium by decantation.

8. A process for refining hydrocarbon oil comprising agitating said oil at 100–250° C. with sodium an amount of alkali metal equal to not less than 20% by weight of said oil at such a rate that said alkali metal is substantially not emulsified, until said oil is substantially chemically neutral, agglomerating the residual alkali metal, hot filtering to remove insoluble treatment by-products and separating refined oil from the remaining sodium by decantation.

9. A process for refining hydrocarbon oil comprising agitating said oil at 100–250° C. with an amount of sodium equal to not less than 20% by weight of the oil at such rate that said sodium is substantially not emulsified, until said oil is substantially chemically neutral, agglomerating the residual sodium, hot filtering to remove insoluble treatment by-products and separating refined oil from the remaining sodium by decantation.

10. A process for refining hydrocarbon oil comprising agitating said oil at 100–250° C. with an amount of sodium equal to 20–30% by weight of the oil at such rate that said sodium is substantially not emulsified, until said oil is substantially chemically neutral, agglomerating the residual sodium, hot filtering to remove insoluble treatment by-products and separating refined oil from the remaining sodium by decantation.

RICHARD SHEPARD VOSE.

## CERTIFICATE OF CORRECTION.

Patent No. 1,952,616. March 27, 1934.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, lines 102 and 103, claim 8, strike out the word "sodium"; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 15th day of May, A. D. 1934.

Bryan M. Battey