

UNITED STATES PATENT OFFICE

2,042,557

REFINING HYDROCARBONS

William J. Sparks, Niagara Falls, N. Y., assignor
to E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

No Drawing. Application May 26, 1933,
Serial No. 673,113

7 Claims. (Cl. 196—23)

This invention relates to the refining of hydrocarbons, and more particularly to the refining of hydrocarbon oils by treatment with alkali metal.

A number of processes for refining hydrocarbon oils such as lubricating oil fractions, transformer oils, and the like, by treatment with alkali metal have been proposed heretofore. One method comprises stirring the oil with finely divided alkali metal and then removing the treated oil from the unreacted metal and reaction by-products by filtration. Although alkali metal treatment results in a highly refined product of excellent color, this process has heretofore been of somewhat limited commercial value. Excellent refining results may be obtained by this method, but at times the desired refining is difficult to attain.

An object of this invention is to provide a controlled process for treating liquid hydrocarbon oils with an alkali metal whereby uniformly excellent results may be obtained regardless of quantities of material treated. Other objects will be apparent hereinafter.

I have discovered that in order to obtain a maximum refining action in processes comprising contacting hydrocarbon oils with alkali metal, followed by filtration, it is necessary to have present a controlled amount of oxygen during the period of contact with the alkali metal. I have further discovered that the degree of refinement and the amount of metal consumed in such process may be controlled by regulating the amount of oxygen supplied to the oil undergoing treatment with the alkali metal. Broadly speaking, my invention comprises simultaneously contacting the hydrocarbon oil with controlled amounts of oxygen or an oxygen-containing gas and with an alkali metal, preferably at a temperature above the melting point of the metal and thereafter filtering to recover refined oil. From the results of my investigations it appears that the degree of refinement obtained, all other conditions being equal, depends upon the amount of oxygen supplied to the reaction mixture, and that the amount of alkali metal which is reacted will vary directly in proportion to the amount of oxygen supplied. Hence, to produce a maximum refinement with minimum consumption of alkali metal, a definite quantity of oxygen must be supplied.

The following example illustrates the effect of the oxygen in refining hydrocarbon oil with alkali metal in accordance with my invention:

Example I

A quantity of a dark colored lubricating oil distillate was placed in a vessel open to the air together with an amount of sodium equal to about 40% by weight of the oil. The mixture was heated to about 230° C. for 3½ hours with sufficient

agitation to keep the alkali metal fairly finely divided. After filtering from the unreacted sodium and insoluble by-products, the oil was practically colorless.

An approximately equal quantity of the same oil was placed in the same vessel with the same proportion of sodium. However, in this case the treating vessel was closed and oxygen was excluded by keeping the mixture under an atmosphere of hydrogen. After agitating the mixture at around 210° C. for a period of 22 hours, substantially no refining action was observed.

In carrying out my invention it is essential that the oxygen be contacted with the oil simultaneously with the alkali metal. As shown by the following example, I have found that treating the oil with oxygen or an oxygen-containing gas prior to or following alkali metal treatment in the absence of oxygen results in substantially no improvement. On the other hand, oxygen present during the alkali metal treatment has a material effect on the oil.

Example II

A quantity of an acid-refined lubricating oil distillate was placed in a closed container and heated therein at 200° C. for 7½ hours while a stream of air was passed over the surface of the oil. Analyses of the off-gas showed that an amount of oxygen equivalent to about 1.4% of the weight of the oil had been absorbed by the oil. At the end of this treatment with air, a quantity of sodium equal to about 20% by weight of the oil was added, the air in the apparatus was displaced by a current of oxygen-free, dry nitrogen, and the mixture was stirred and treated under the nitrogen atmosphere at 200° C. After 6½ hours of treatment in the nitrogen atmosphere there was no evidence of any refining action.

Another portion of the same acid-refined lubricating oil distillate was agitated with 20% of its weight of sodium at 200° C. under an atmosphere of nitrogen for 24 hours. At the end of this period there was no evidence of any refining action, the treated oil being dark brown in color.

The dark brown oil was filtered from the unreacted sodium and was then treated by blowing with air for 24 hours. This treatment failed to improve the color to any noticeable extent.

A further portion of the above-mentioned distillate was placed in a closed vessel with about 20% of its weight of sodium. The mixture was heated to about 200° C. while a stream of air was passed over the liquid and the mixture was agitated so as to maintain the sodium in a finely divided condition. At the end of 6 hours and 20 minutes the treated oil was filtered from the sodium and reaction products and compared with a sample of the untreated oil distillate.

The results of this comparison are shown in the following table:

Table I

Test	Treated oil	Untreated oil
Color (Saybolt).....	20	Yellow
Slight oxidation No.....	6	20
Viscosity 100° F. (Saybolt).....	141	155

The following examples further illustrate my invention:

Example III

A series of runs was carried out to refine the acid-treated distillate described in Example II, using varying proportions of air. In each run approximately 500 cc. of the oil was placed in a closed container together with 100 grams of sodium. The container was provided with means for passing air through the space above the oil. The refining was carried out by heating the mixture of oil and sodium to 200-205° C. with thorough agitation, while air was passed through the apparatus at a rate which was held constant in each run. The air leaving the apparatus was analyzed to determine the amount of oxygen absorbed by the oil-sodium mixture. When a filtered sample of the oil was found to have a substantially water white color, the oil was removed from the reaction apparatus and filtered to separate it from the unreacted sodium and reaction by-products. The following results were obtained:

Table II

Run	Rate of flow of air (N. P. T.)	Oxygen absorbed	Refining time	Saybolt color of product
	cc./min.	Grams	Minutes	
1	10.9	3.24	1240	18
2	11.5	3.92	1240	18
3	36.0	7.95	330	20
4	109.0	9.10	210	20
5	179.0	9.6	210	20
6	190.0	10.9	225	24

Example IV

Five hundred cc. of the acid-treated oil distillate described in Example II was agitated with sodium under an atmosphere of pure oxygen at a temperature of 200 to 205° C. for 450 minutes. After unreacted metal and reaction by-products has been filtered out, the oil was substantially neutral and had a Saybolt color of 24 and a Slight oxidation number of 4.0. During the run 8,900 cc. of oxygen, calculated at normal temperature and pressure was put through the apparatus and 12.6 grams of oxygen was absorbed by the reaction mixture.

In practicing my invention the amount of oxygen absorbed by the reaction mixture during the refining operation may be varied between wide limits, depending upon the nature of the oil to be refined and the desired degree of refining. In most cases, the amount of sodium consumed will vary directly with the amount of oxygen absorbed by the reaction mixture. In most practical refining operations, it will be necessary to limit the oxygen consumption in order to avoid undue loss of the refining agent; but if too little oxygen is absorbed, the desired refining effects will not be obtained. In any case, the optimum amount of oxygen absorption can be determined by simple trials. When

the relationship between the oxygen absorption, alkali metal consumption, and refining effect has been established for a particular hydrocarbon oil, uniform results may be obtained by controlling the oxygen absorption in relation to the other factors; i. e., temperature, refining time, and proportion of alkali metal.

Various methods may be used for varying or controlling the rate of oxygen absorption. The oxygen may be diluted with an inert gas; for example, by the use of air. By varying the method of applying the oxygen or oxygen-containing gas to the reaction mixture, varying amounts of oxygen may be made to be absorbed by the oil. For example, by bubbling the gas through the reaction mixture the rate of oxygen absorption will be considerably greater than when the gas is simply passed over the surface of the oil. Likewise the oxygen absorption rate will vary with the rate of flow of the gas through the refining apparatus.

The amount of oxygen absorbed will also vary with the temperature at which the refining operation is carried out; at higher temperatures somewhat more oxygen will be absorbed. In any case, under constant conditions of temperature, pressure, degree of agitation, proportion of alkali metal, and time of refining, consistently uniform results in the refining of a given hydrocarbon oil may be obtained by maintaining a constant rate of flow of oxygen or a selected oxygen-containing gas; e. g., air, through the refining apparatus.

In general, an increase in the rate of oxygen absorption will be accompanied by an improved degree of refinement and will also result in a somewhat higher consumption of the alkali metal employed.

The amount of oxygen to be applied will depend upon the factors mentioned above, the nature of the oil and the degree of refinement desired. Obviously, if the amount of oxygen absorbed during the process is very small, the refining effect will be proportionately poor, while if excessive amount of oxygen is used, undue oxidation of the oil and metal will occur. I prefer to use such quantity of oxygen that the amount absorbed is equal to about 1.0 to 5.0% by weight of the oil treated.

In practicing my invention it is not necessary to introduce oxygen throughout the entire treatment with the alkali metal, provided that the oxygen is applied in the presence of the alkali metal, and a sufficient quantity of oxygen is absorbed to give the desired refining result. Also, in order to obtain the best results, I prefer to have oxygen present in substantial amounts at the end of the refining period, that is, up to the time that the refined oil is separated from unreacted metal and reaction by-products.

One modification of my invention comprises treating the oil with an excess of alkali metal for a suitable period of time in the presence of little or no oxygen and then continuing the treatment for a short time in the presence of oxygen. This method produces substantially the same results as when oxygen is applied throughout the entire run, provided that alkali metal is always present when the oxygen is applied.

The temperatures which have been satisfactory heretofore for refining hydrocarbon products with alkali metals are suitable for my process. While alkali metal will slowly act upon the oil at temperatures as low as 10° C., I prefer to

operate above the melting point of the metal and below the cracking temperature of the oil; e. g., 100 to 250° C. Between these limits, an increase in operating temperature will generally shorten the time required to attain a desired refining effect.

While I prefer to use pure oxygen or oxygen mixed with an inert gas only, small amounts of reactive gases, such as water vapor or CO₂ are not deleterious. For example, ordinary air containing small amounts of carbon dioxide and saturated with water vapor at atmospheric temperature may be used with practically the same results that are obtained with dry carbon dioxide-free air. The effect of such reactive impurities in the air is to somewhat increase the consumption of alkali metal but it has very little effect upon the combined refining action of the oxygen and alkali metal.

Although I have demonstrated the effectiveness of the presence of oxygen in controlled amounts in refining hydrocarbon oils with alkali metals, it appears that some reaction usually occurs between the alkali metals and hydrocarbon oils, even in the absence of oxygen. However, the reaction in the absence of oxygen often is either not sufficiently complete or the nature of the reaction is not of the proper sort, with the result that a light colored, highly refined oil is not always obtained when the oil is filtered to separate unreacted metal and insoluble reaction by-products. On the other hand, my process enables uniform production of light colored or colorless oil in practically all cases and the degree of refining may be effectively controlled by controlling the amount of oxygen absorbed by the reaction mixture.

I claim:

1. A process for refining a hydrocarbon oil comprising treating said oil simultaneously with an alkali metal and oxygen in such manner that an amount of oxygen equivalent to 1.0 to 5.0% by weight of the oil is absorbed during the treating period and filtering the mixture to recover refined oil.

2. A process for refining a hydrocarbon oil comprising treating said oil simultaneously with sodium and air at 100 to 250° C. in such manner

that an amount of oxygen equivalent to 1.0 to 5.0% by weight of the oil is absorbed during the treating period and filtering the mixture to recover refined oil.

3. A method for refining a hydrocarbon oil comprising agitating said oil with sodium at 100 to 250° C. and simultaneously contacting the mixture of oil and sodium with such amounts of air that the mixture absorbs an amount of oxygen equal to 1.0 to 5.0% of the weight of said oil and subsequently filtering to recover refined oil.

4. A method for refining a hydrocarbon oil comprising agitating said oil with an excess of sodium at 100 to 250° C. in the substantial absence of oxygen, thereafter supplying sufficient air to the mixture, in the presence of the unreacted sodium, to cause the absorption of a quantity of oxygen equal to 1.0 to 5.0% of the weight of the oil and subsequently filtering to recover refined oil.

5. A process for refining a hydrocarbon oil comprising treating said oil simultaneously with a molten alkali metal and oxygen in such manner that an amount of oxygen is absorbed which is equivalent to not less than about 1% by weight of the oil but less than that amount required to oxidize the total alkali metal present and subsequently filtering the mixture to recover refined oil.

6. A process for refining a hydrocarbon oil comprising treating said oil simultaneously with molten sodium and air in such manner that an amount of oxygen is absorbed which is equivalent to not less than about 1% by weight of the oil but less than that amount required to oxidize the total sodium present and subsequently filtering the mixture to recover refined oil.

7. A process for refining a hydrocarbon oil comprising treating said oil simultaneously with molten sodium and air at a temperature of 100-250° C. in such manner that an amount of oxygen is absorbed which is equivalent to not less than about 1% by weight of the oil but less than that amount required to oxidize the total sodium present and subsequently filtering the mixture to recover refined oil.

WILLIAM J. SPARKS.