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OXIDATION OF HYDROCARBON OILS

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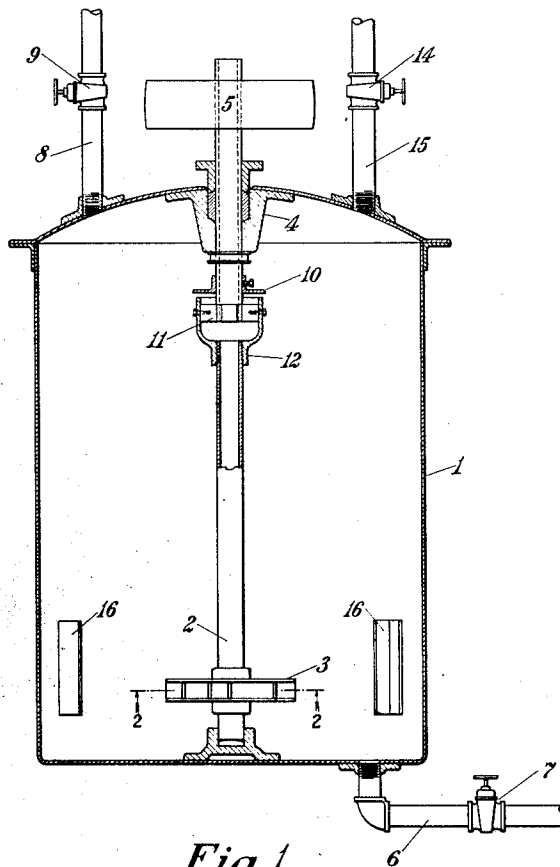


Fig. 1

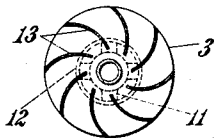


Fig. 2

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By his attorney J.R. Squair.

UNITED STATES PATENT OFFICE.

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OXIDATION OF HYDROCARBON OILS.

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This invention relates to the treatment of hydrocarbons such as occur in mineral oils, and comprises subjecting hydrocarbons, and particularly high boiling paraffin hydrocarbons, to an intensive oxidation at an elevated temperature.

One object of my invention is to improve the efficiency of processes of cracking high boiling petroleum fractions in the production of gasolene and other low boiling paraffin oils.

Another object of my invention is to provide a process of oxidizing difficultly oxidizable hydrocarbons which shall be so accurately controllable as to permit of the recovery of the relatively unstable oxygen derivatives of the hydrocarbons.

It is well known that mineral oils, such as petroleum and fractions obtained in the distillation thereof, are slowly oxidized by contact with air, this oxidation being hastened by operating at high temperatures or with the aid of catalysts. Heat is always generated by this reaction, the temperature reached by the reaction mass being dependent upon the conditions under which the process is carried out and on the rate at which the heat is dissipated.

The treatment of mineral oils with air (or oxygen) as heretofore carried out has involved little or no special agitation of the oil, the agitation caused by the air bubbles being relied upon to bring about contact between the gas and the liquid.

According to my invention the air is comminuted and disseminated throughout the oil in such an extreme degree of subdivision as to approach molecular dispersion. By proceeding in this way the speed of the reaction is multiplied many times as compared with a reaction carried out at the same temperature with the ordinary stirring. Furthermore, this new procedure enables me to bring about the rapid oxidation of paraffins and other hydrocarbons at temperatures considerably below those which have heretofore been considered practicable. By thus lowering the reaction temperature, some products which would be decomposed at the higher temperatures are sufficiently stable at the lower temperature to permit of their being recovered from the oxidized oil; this is particularly the case with certain aldehydes resulting from the partial oxidation of hydrocarbons.

I preferably effect the subdivision of the air and its dissemination through the oil by an efficient stirrer of the Witt type which is described in *Berichte der Deut. Chem. Gesell.* Vol. 26, page 1696, wherein the air is introduced through the stirrer arms. A more elaborate form of stirrer of this type is shown in the U. S. patent to Thoens No. 641,561. With a stirrer of this type the oil is drawn into the stirrer and ejected at high velocity through the body of the oil, entraining air in its passage, and mingling the entrained air with the body of oil. The manner in which I operate a stirrer of this kind differs greatly, however, from the customary operation of such stirrers in that instead of a speed of several hundred revolutions per minute, I rotate the stirrer at several thousand revolutions per minute.

The oil to be cracked or oxidized may, for example, be the residue remaining after the removal of the gasolene, or the gasolene and kerosene, fractions—that is the type of oil that is commonly used in “cracking” processes. The temperature at which the treatment of the oil is carried out will depend upon the product which it is desired to obtain. For example in the manufacture of gasolene from a high boiling oil of the character above described I preferably operate at a temperature between about 370 and 425° C. (that is between 700 and 800° F.); in certain cases I may operate at temperatures as low as 330 or 300° C. The temperature required may be said in general to depend on the reactivity of the oil and the character of the cracked distillate desired, a higher temperature being required when more severe cracking is to be effected.

At such temperatures pressure is, of course, necessary to maintain the heavier compounds mostly in the liquid state, about 300 pounds per square inch being required at temperatures of about 400° C. At the above temperatures and pressures the desired gasolene fraction distils over and is collected in a reservoir also under pressure. The pressure required depends on the volatility of the oil or mixture of oils being treated, in general sufficient pressure being used to maintain most of the oil in the liquid state.

The process may be illustrated in greater detail by the following example:—A convenient quantity of petroleum oil from

which the gasoline and kerosene fractions have been removed by a preliminary distillation is placed in a still adapted to withstand high pressure and provided with a Witt type stirrer and communicating through a reflux condenser with a suitable collector also designed to withstand high pressure. The oil is first heated externally to a temperature of about 400° C.; air is then introduced by rotating the stirrer at a high speed, the air being conducted to the stirrer under a pressure substantially the same as that which exists over the oil. With a stirrer of the above type in which the total length of the two arms is from 1 to 1½ inches (the operation in this case being on a small scale) good results may be obtained by rotating the stirrer at 5,000 R. P. M. It will be understood, of course, that the optimum speed is usually dependent on the design and efficiency of the stirrer which is used. The process is carried out continuously, fresh oil being fed in as required to maintain a suitable body of oil in the apparatus. After the oxidation has once started the external heating is stopped, the temperature of the apparatus and the progress of the reaction being regulated by the rate of admission of the air. In some cases the reaction becomes so vigorous that it is necessary to apply a cooling medium to the reaction vessel to maintain the proper temperature. In other cases it may be desirable to use a higher percentage of oxygen than is contained in ordinary air.

As the reaction proceeds gasoline is formed and passes through the condenser to the collector where it is condensed under pressure, while unchanged oil which may be momentarily vaporized is condensed and caused to flow back into the body of oil being treated.

The reactions which ensue when a mineral oil is treated with oxygen at a high temperature of say from 300 to 500° C. are probably as follows:—Some of the molecules of the oil are first oxygenated, and then the oxygenated molecules decompose, or the non-oxygenated molecules which are brought in intimate contact with those being oxidized may be decomposed. In either case smaller and more volatile molecules result and distill off through the condenser.

A suitable type of apparatus for carrying out the above described process is illustrated in the accompanying drawings, wherein—

Figure 1 is a central vertical sectional view of the apparatus; and Figure 2 is a horizontal section on line 2—2 of Figure 1.

Figure 1 represents a vessel for holding the liquid to be treated in which is mounted a tubular shaft 2 carrying a fluid distributor 3. The shaft 2 passes thru a stuffing box 4 in the cover of the vessel 1, and carries on its upper part a pulley 5. The vessel 1 has

an outlet 6 provided with a valve 7, and the cover of the vessel 1 is provided with an inlet 8 with a valve 9, and a vapor outlet 15 provided with a valve 14. Vertical strips 16 are attached to the inside of the vessel 1 to prevent swirling of the liquid in the vessel when the fluid distributor is rotated.

The distributor is formed of the turbine blades 13. The lower section of the broken agitator shaft 2, carries at its upper end a cup-shaped member 12 which is secured through a spider or cross-shaped member 11 to the lower end of the upper shaft section on which the pulley 5 is mounted. There is thereby provided an inlet to the fluid-distributor at this point. 10 represents a disk or other suitable closure adjustable on the upper section of the shaft to control the aperture as may be desired, or to close it entirely. Obviously, any other construction accomplishing the same result may be used. Oxygen or air is introduced into the oil either through the upper section of the hollow shaft 2 or through the cup-shaped member 12 leading into the lower section of the shaft 2 and thence to the distributor 3.

Where the operation is carried on for the purpose of producing gasoline from high boiling paraffins about 10% of the oil is oxidized, the oxidation products being chiefly carbon monoxide, carbon dioxide and water. These products being in the vapor phase are immediately removed from the field of the reaction and thus permit the process to be carried on for long periods without the formation of solid residues in the still.

The chief advantages of my new process as applied to the cracking of oils are increased heat economy and the reduction in the time required for cracking a given quantity of oil with a corresponding increase in plant capacity.

I claim:

1. The process of treating a high boiling hydrocarbon oil which comprises forcing the liquid centrifugally outward through an orifice or opening below the surface of a body of said liquid at a temperature between 300 and 500° C., which orifice or opening communicates with a supply of an oxygen-containing gas, whereby oxygen is entrained and drawn into the body of liquid and whereby an intimate mixture of the liquid and the oxygen-containing gas is brought about.

2. A process as defined in claim 1 in which barriers are interposed in the path of the currents of liquid set up in the body of liquid by centrifugally forcing liquid into said body.

3. The process of cracking a high boiling fraction of mineral oil which comprises subjecting said fraction in the liquid state at a temperature between about 300 and 500° C.

to the action of air disseminated throughout the oil in a state of extremely fine subdivision, the degree of subdivision being equal to that obtainable by mixing the air with the oil by means of a Witt type stirrer, one and one-half inches in diameter, rotated at a speed of more than 3000 revolutions per minute.

4. The process of treating a high boiling mineral oil which comprises maintaining a body of oil at a temperature between about 300 and 500° C. and under sufficient pressure to prevent rapid vaporization of said oil, continuously introducing air into said body of oil to facilitate the decomposition thereof into more volatile products, continuously withdrawing said volatile products, and replenishing the body of oil with fresh oil, the air being introduced in the form of minute bubbles of a size obtainable by introducing the air with a Witt type stirrer of 1½ inches in diameter rotated at a speed greater than 3000 revolutions per minute.

5. A process of oxidizing a hydrocarbon oil which comprises injecting finely divided, oxygen-containing gas into a body of such oil below the surface thereof in narrow rotating streams, the degree of subdivision of the gas being at least as great as that obtainable by mixing the gas with the liquid by means of a Witt type stirrer, one and one-half inches in diameter, rotated at a speed of 3000 revolutions per minute.

6. The method of effecting oxidation of a body of hydrocarbon oil which comprises forcing the liquid centrifugally outward from near the center of said body at a temperature of between 300° and 500° C. and causing said traveling liquid to entrain an oxygen-containing gas whereby an intimate mixture of the liquid and the gas is brought about.

7. A process of oxidizing a hydrocarbon oil which comprises heating a body of such oil to a temperature between 300° and 500° C. and injecting finely divided oxygen-containing gas into the heated body of oil below the surface thereof through an orifice rotating in excess of a thousand revolutions per minute.

8. A process of oxidizing mineral oil which comprises heating a body of said oil to a temperature between 300° and 500° C., circulating a portion of said oil from the bottom of said body to the top and back to the bottom again, permitting said circulating oil to come in contact with a body of gas containing free oxygen, whereby said gas is entrained in said oil, and injecting said oil and entrained gas through a rotating orifice below the surface of the body of oil.

9. In a process of oxidizing a liquid hydrocarbon oil, the steps which comprise forcing the liquid in narrow rotating streams below the surface of the body of the liquid, supplying an oxygen containing gas to the streams, and thereby effecting such an intimate mixture of liquid and gas that the degree of subdivision of the gas is at least as great as that obtainable by mixing the gas with the liquid by means of a Witt type stirrer, one and one-half inches in diameter, rotated at a speed of 3000 revolutions per minute.

10. A process of oxidizing mineral oil which comprises injecting finely divided oxygen containing gas into a heated body of the oil below the surface thereof in streams rotating in excess of a thousand revolutions per minute.

11. The process of treating a high-boiling hydrocarbon liquid at temperatures between 370° C. and 425° C., with air dispersed in the liquid to the degree obtainable by means of a Witt type stirrer, 1½ inches in diameter, rotated at a speed in excess of 1000 revolutions per minute.

12. The process of cracking high-boiling fractions of mineral oil which comprises oxidizing the fractions at temperatures between 300° and 500° C., with air comminuted and disseminated throughout the fractions in such an extreme degree of subdivision as to approach molecular dispersion and equal to that obtainable by means of a Witt type stirrer, 1½ inches in diameter, rotated at a speed in excess of 1000 revolutions per minute.

13. The process of treating a high-boiling fraction of a mineral oil which comprises forcing liquid of which said fraction is composed through an orifice or opening below the surface of a body of said high-boiling fraction maintained at a temperature between 370° and 425° C., which orifice or opening communicates with a supply of an oxygen-containing gas, and dispersing the gas in the oil to a degree equal to that obtainable by means of a Witt type stirrer, 1½ inches in diameter, rotated at a speed in excess of 1000 revolutions per minute.

14. The process of treating a high-boiling hydrocarbon which comprises subjecting said hydrocarbon in the liquid state at a temperature between about 370° and 425° C. to the action of air disseminated throughout the liquid in a state of extremely fine subdivision, the degree of subdivision being at least as great as that obtainable by mixing the air with the liquid by means of a Witt type stirrer, 1½ inches in diameter, rotated at a speed of more than 3000 revolutions per minute.

In testimony whereof I affix my signature.
EBENEZER EMMET REID.