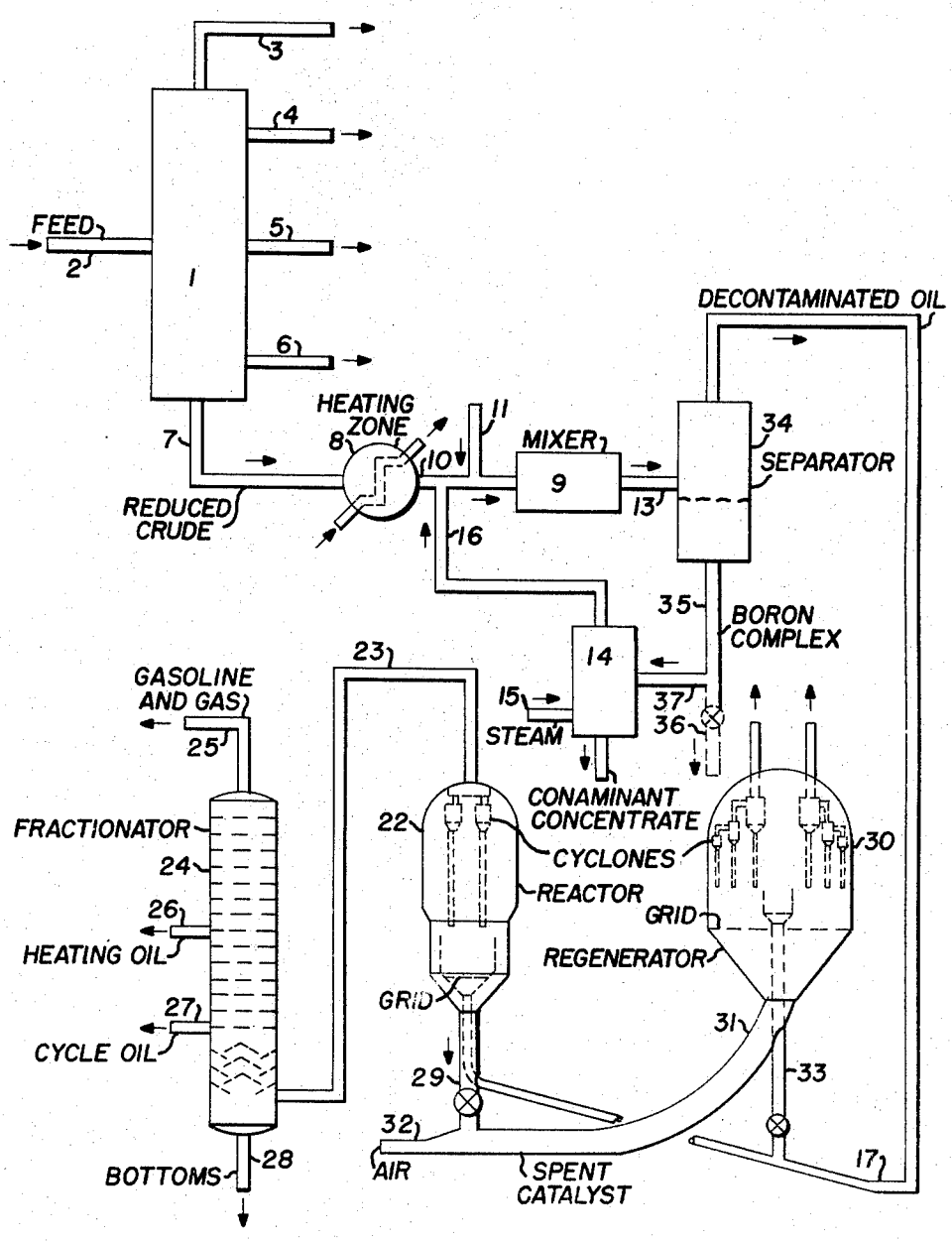
June 16, 1959 W. J. MATTOX 2,891,004

PROCESS FOR REMOVAL OF METAL CONTAMINANTS FROM HIGH BOILING OILS BY USE OF BORON COMPOUNDS

Filed Oct. 19, 1955



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United States Patent Office 2,891,004 Patented June 16, 1959

2,891,004

PROCESS FOR REMOVAL OF METAL CONTAMINANTS FROM HIGH BOILING OILS BY USE OF BORON COMPOUNDS

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Application October 19, 1955, Serial No. 541,391

5 Claims. (Cl. 208—251)

The present invention is concerned with an improved process for the removal of undesirable constituents from petroleum oils, particularly from petroleum oils remaining after distillation of volatile components. The invention is more particularly concerned with an improved process for the preparation of satisfactory feed stocks for a fluid catalytic cracking operation. In accordance with the present invention, undesirable iron, vanadium and nickel constituents are removed from petroleum oils, particularly from high boiling petroleum oils by an operation which comprises treating these oils with a compound of boron such as boron oxide and boric acid followed by the removal of these constituents.

The present invention is a continuation-in-part of U.S. Serial No. 258,624, filed November 28, 1951, now abandoned.

It is well known in the art to treat mineral oils by various processes in order to remove undesirable constituents from these oils. For example, it is known to employ light hydrocarbon solvents, as for example, hydrocarbons such as propane and butane in order to remove undesirable constituents, such as, asphaltic constituents therefrom. In these operations various temperatures and pressures are employed, as well as, various solvent to oil ratios. It is also known in the art to use various other processes for the preparation of high quality oils such as those for the removal of gum and ash-forming constituents therefrom. These processes have generally been directed toward the preparation of satisfactory high boiling feed stocks for a fluid catalytic cracking operation. In a catalytic cracking operation, the removal of iron, nickel and vanadium compounds from feed stocks is desirable since the use of feed stocks, as for example reduced crudes, containing these undesirable constituents is prohibitive due to the excessive formation of dry gas, carbon and ash.

It has now been discovered that undesirable metals or metal compounds such as various oxides or salts of iron, vanadium, nickel, sodium, and calcium may be efficiently removed from feed stocks of the reduced crude type, providing the crude is treated with a boron compound, preferably at elevated temperatures. The process of the present invention may be readily understood by reference to the drawing illustrating one embodiment of the same.

Referring specifically to the drawing, a feed oil, as for example, a West Texas crude, is introduced into distillation zone 1 by means of feed line 2. Temperature and pressure conditions are adjusted in zone 1 to secure the desired fractionation of the crude oil. Light hydrocarbon gases are removed overhead by means of line 3; a lower boiling hydrocarbon fraction is removed by means of line 4, a higher boiling hydrocarbon fraction is removed by means of line 5, and a somewhat higher boiling fraction is removed by means of line 6. A fraction boiling in the reduced crude boiling range, as for example, in the range above about 600° to 700° F., preferably boiling in the range above 750° F., is segregated as a bottoms fraction by means of line 7. It is to be understood that zone 1

may comprise any suitable number and arrangement of distillation zones or stages.

In accordance with the present invention, the high boiling oil is raised to an elevated temperature in heating zone 8 and passed to treating and mixing zone 9 by means of line 10 wherein it is contacted with a boron compound introduced into zone 9 by means of line 11. It is to be understood that treating and mixing zone 9 likewise may comprise any suitable number and arrangement of stages.

The boron compound may be introduced, through lines 11 and 10, to a mixer 9 as a slurry in a portion of the reduced crude or other suitable oil or as an oil-insoluble molten phase. Mixer 9 is of such design as to provide intimate contact of the oil and molten boron-containing compound and of such capacity as to permit adequate reaction time between metal-containing hydrocarbons and the boron additive. The effluent from mixer 9 is passed through line 13 to separator 34 held at an elevated temperature of about 300 to 500° F. or sufficient to maintain the components in a fluid condition and thereby facilitate separation and settling of the boron complex. The boron complex, which now contains metal contaminants, is withdrawn through line 35 and either discharged through line 36 or passed through line 37 to steam stripping zone 14 for boron recovery. Decomposition of the boron complex in zone 14 and volatilization of the boron oxide by means of steam introduced through line 15 permits return of a major portion of the boron to the system through line 16.

The treated oil free of undesirable iron, vanadium and nickel compounds is removed from zone 14 by means of line 17 and introduced into a fluid catalytic cracking operation. The fluid catalytic cracking plant is composed of three sections: cracking, regeneration, and fractionation. The cracking reaction takes place continuously in one reactor, the spent catalyst being removed continuously for regeneration in a separate vessel, from which it is returned to the cracking vessel. Continuity of flow of catalyst as well as of oil is thus accomplished, and the characteristic features of fixed-bed designs involving the intermittent shifting of reactors through cracking, purging, and regeneration cycles are eliminated.

Regenerated catalyst is withdrawn from the regenerator and flows by gravity down a standpine, wherein a sufficiently high pressure head is built up on the catalyst to allow its injection into the fresh liquid oil stream. The resulting mixture of oil and catalyst flows into the reaction vessel, in which gas velocity is intentionally low, so that a high concentration of catalyst will result. The cracking that takes place results in carbon deposition on the catalyst, requiring regeneration of the catalyst. The cracked product oil vapors are withdrawn from the top of the reactor after passing through cyclone separators to free them of any entrained catalyst particles, while the spent catalyst is withdrawn from the bottom of the reactor and is injected into a stream of undiluted air which carries the catalyst into the regeneration vessel. The products of combustion resulting from the regeneration of the catalyst leave the top of this vessel and pass through a series of cyclones where the bulk of the entrained catalyst is recovered. The regenerated catalyst is withdrawn from the bottom of the vessel to complete its cycle.

Again referring specifically to the drawing, in accordance with a preferred adaptation of the present invention, the treated oil removed by means of line 17 is introduced into a catalytic cracking zone 22.

Temperature and pressure conditions in cracking zone 22 are adjusted to secure the desired conversion of the feed oil. Cracked products are removed overhead from zone 22 by means of line 23 and passed into a fractionation zone 24. Temperature and pressure conditions in

fractionation zone 24 are adjusted to remove overhead by means of line 25 hydrocarbon constitutents boiling in the gasoline and lower boiling ranges. This stream is passed to a stabilizing unit where a gasoline fraction of the desired volatility is segregated. A heating oil fraction is removed by means of line 26 while a fraction boiling in the cycle oil boiling range is removed by means of line 27. A bottoms fraction is removed by means of line 28 and handled as desired. Spent catalyst is removed from the bottom of zone 22 by means of line 29 and passed into a regeneration zone 30 by means of line 31. Sufficient air is introduced into the system by means of line 32. Regenerated catalyst is removed from the bottom of zone 30 by means of line 33 and passed to the reactor along with the feed by means of line 17.

The invention is broadly concerned with the removal of undesirable materials from petroleum oils, particularly from petroleum oils boiling in the reduced crude boiling range. Petroleum oils treated in accordance with the present invention are particularly adapted as feed stocks for a catalytic cracking reaction. Although the invention may be adapted for the treatment of mineral oils boiling over wide ranges as pointed out above, it is particularly adapted for the treatment of oils boiling above about 750° F., preferably boiling above about 860° F.

Various compounds of boron as well as boron may be employed, as for example boron oxide and boric acid. The boron compounds may be added in solid or in liquid form and the thermal treatment carried out in coils, fractionating columns or in fluid beds. The boron compound may be supported on various porous materials by impregnation or steam volatilization. Molten boric acid may also be utilized. The amount of boron compound added is preferably in the range from about .5 to 3% by weight of the feed oil. It is preferred to employ from about 1% to 1½% of the boron compound by weight. The temperature of contact should be in the range from about 250° to 850° F. A preferred range for contacting the boron compound with the feed oil is in the range from about 600 to 700° F.

As discussed above, the invention is particularly concerned with an improved operation which comprises the treatment of a reduced crude by contacting it with boron or with a boron compound and then to use the treated stock to secure an improved fluid catalytic cracking operation. It is well known in the art to produce cracked naphthas by a fluidized solids catalytic operation wherein the cracked product comprises constituents boiling in the motor fuel boiling range, as for example, below about 430° F. The cracked product also comprises normally gaseous constituents, as for example, those containing three carbon atoms and less in the molecule. The fluidized solids technique for processing feed fractions, as for example, gas oils, heavy residuums and other feed stocks for the production of hydrocarbon fractions boiling in the motor fuel boiling range is a conventional one. As pointed out heretofore, the system of a fluidized solids technique comprises a reaction zone and a regeneration zone, employed in conjunction with a fractionation zone. The reactor and the catalyst regenerator are arranged at approximately an even level. The operation of the reaction zone and the regeneration zone is conventional, which preferably is as follows:

An overflow pan is provided in the regeneration zone at the desired catalyst level. The catalyst overflows into a withdrawal line which preferably has the form of a U-shaped seal leg connecting the regeneration zone with the reaction zone. The feed stream introduced is usually preheated to a temperature in the range from about 500° to 650° F. in exchangers in heat exchange with regenerator flue gases which are removed overhead from the regeneration zone, or with cracked products. The heated feed stream is withdrawn from the exchangers and introduced into the reactor. The seal leg is usually sufficiently below the point of feed oil injection to prevent oil vapors from backing into the regenerator in case of normal surges. Since there is no restriction in the overflow line from the regenerator, satisfactory catalyst flow will occur as long as the catalyst level in the reactor is slightly below the catalyst level in the regenerator when vessels are carried at about the same pressure. Spent catalyst from the reactor flows through a second U-shaped seal leg from the bottom of the reactor into the bottom of the regenerator. The rate of catalyst flow is controlled by injecting some of the air into catalyst transfer line to the regenerator.

The pressure in the regenerator may be controlled at the desired level by a throttle valve in the overhead line from the regenerator. Thus, the pressure in the regenerator may be controlled at any desired level by a throttle valve which may be operated, if desired, by a differential pressure controller. If the pressure differential between the two vessels is maintained at a minimum, the seal legs will prevent gases from passing from one vessel into the other in the event that the catalyst flow in the legs should cease.

The reactor and the regenerator may be designed for high velocity operation involving linear superficial gas velocities of from about 2.5 to 4 feet per second. However, the superficial velocity of the upflowing gases may vary from about 1–5 and higher. Catalyst losses are minimized and substantially prevented in the reactor by the use of multiple stages of cyclone separators. The regeneration zone is provided with cyclone separators. These cyclone separators are usually from 2 to 3 and more stages.

Distributing grids may be employed in the reaction and regeneration zones. Operating temperatures and pressures may vary appreciably depending upon the feed stocks being processed and upon the products desired. Operating temperatures are, for example, in the range from about 800° to 1000° F., preferably about 850°–950° F., in the reaction zone. Elevated pressures may be employed, but in general pressures below 100 lbs. per sq. in. gauge are utilized. Pressures generally in the range from 1 to 30 lbs. per sq. in. gauge are preferred. A catalyst holdup corresponding to a space velocity of 1 to 20 weights per hour of feed per weight of catalyst is utilized. A preferred ratio is 2 to 4. Catalyst to oil ratios of about 3 to 10, preferably about 6 to 8 by weight are used.

The catalytic materials used in the fluidized catalyst cracking operation, in accordance with the present invention, are conventional cracking catalysts. These catalysts are oxides of metals of groups II, III, IV and V of the periodic table. A preferred catalyst comprises silica-alumina wherein the weight percent of the alumina is in the range from about 5 to 20%. Another preferred catalyst comprises silica-magnesia where the weight percent of the magnesia is about 5% to 20%. The size of the catalyst particles is usually below about 200 microns. Usually at least 50% of the catalyst has a micron size in the range from about 20–80. Under these conditions with the superficial velocities as given, a fluidized bed is maintained where in the lower section of the reactor, a dense catalyst phase exists while in the upper area of the reactor a dispersed phase exists.

The above described operation, as pointed out, has not been entirely satisfactory for cracking heavy oils such as a reduced crude due to excessive formation of dry gas, carbon, and ash on the catalyst. However, by combining the boron treating stage with the catalytic cracking stage, an improved operation results when using feed stocks of this character.

What is claimed is:

1. An improved process for the removal of iron, nickel and vanadium contaminants from a hydrocarbon oil boiling above about 750° F. which comprises contacting said oil with from about 0.5 to about 3% by weight, based upon the oil, of a boron compound selected from the

group consisting of boron oxide and boric acid at a temperature above about 250° F.; separately recovering a boron complex and decontaminated oil; decomposing said boron complex with steam; and recovering at least a portion of said boron compound.

2. A process as defined by claim 1 wherein said oil is contacted with said boron compound at a temperature in the range of from about 600° F. to about 800° F.

3. A process as defined by claim 1 wherein said oil is contacted with from about 1% to about 1.5% of said boron compound.

4. A process as defined by claim 1 wherein said boron compound is boron oxide.

5. A process as defined by claim 1 wherein said boron compound is boric acid.

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