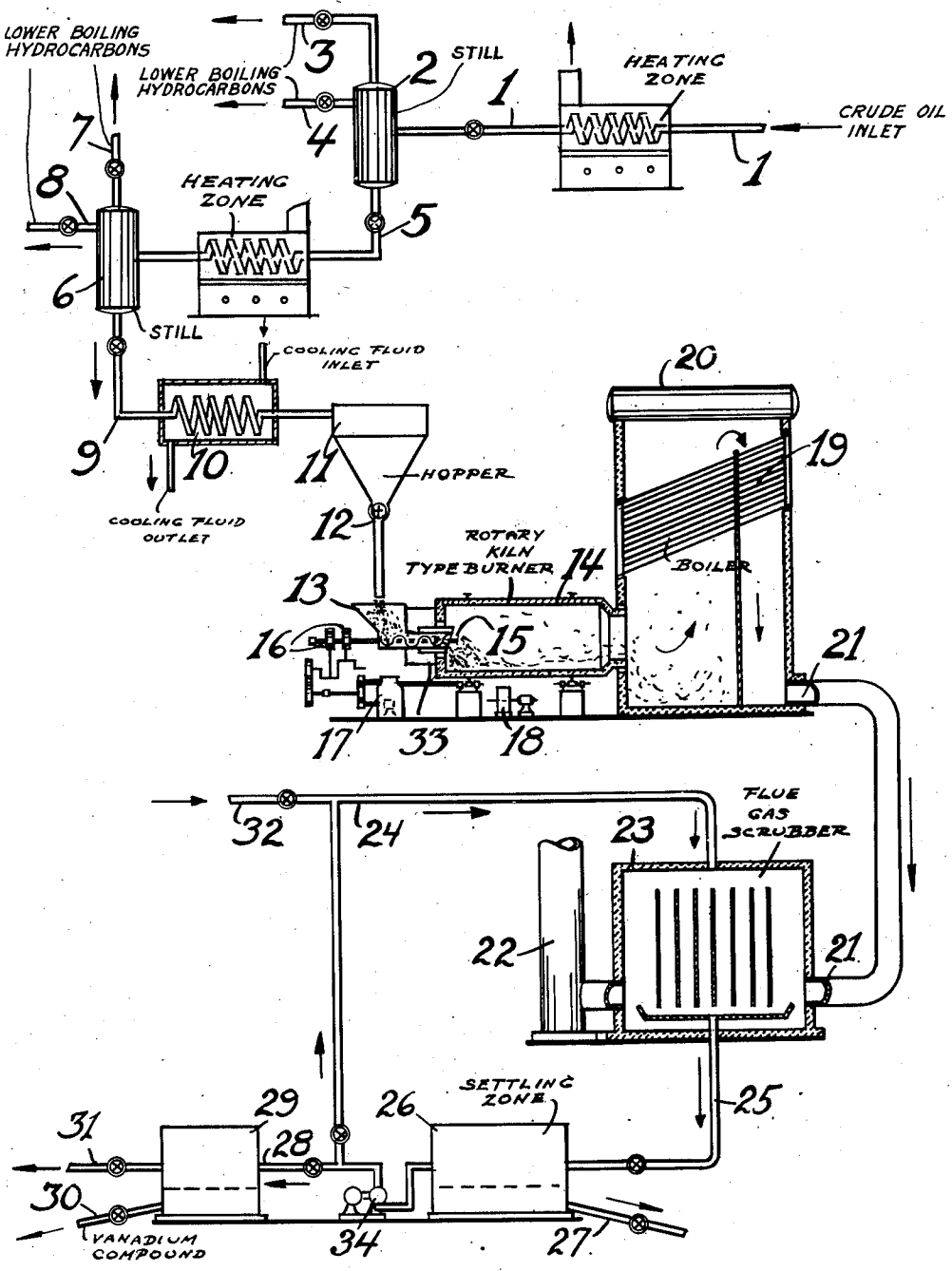
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RECOVERY OF VANADIUM

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RECOVERY OF VANADIUM

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The present invention is concerned with the recovery of vanadium. The invention more particularly relates to a process for the segregation and recovery of vanadium from petroleum oils. In accordance with the present invention, vanadium is recovered from petroleum oils by segregating a high boiling solid or semi-solid fraction from the feed oil, followed by burning and oxidizing the segregated solid fraction under controlled conditions.

It is known in the art that vanadium is present in various petroleum oils. However, due to the fact that the concentration of the same is relatively small, operations directed for its recovery from these oils have not been commercially successful. I have, however, now discovered an operation by which the vanadium may be readily and efficiently recovered, utilizing a particular arrangement and sequence of distillation and oxidizing stages. The process of my invention may be readily understood by reference to the drawing illustrating one particular embodiment of the same.

Referring specifically to the drawing, it is assumed for the purpose of description that the feed oil is a Venezuelan crude oil. The feed oil is introduced into initial heating and distillation zone 2 by means of feed line 1. Temperature and pressure conditions in zone 2 are adapted to remove the relatively lower boiling hydrocarbon constituents overhead by means of lines 3 and 4 respectively and to remove by means of line 5 a reduced crude fraction. This fraction is passed into a secondary heating and distillation zone 6. For purposes of description it is assumed that the secondary distillation zone 6 comprises a vacuum distillation or equivalent zone. Temperature and pressure conditions in zone 6 are adapted to remove relatively low boiling constituents by means of lines 7 and 8 and to segregate a high boiling bitumen fraction which is removed as a bottoms product by means of line 9. This fraction is cooled in cooling zone 10 and solidified by contact with water as it passes to the storage pile 11. The solid material is withdrawn from zone 11 by means of line 12 which may comprise any suitable conveying means, and passed to feed hopper 13.

The material is passed into rotary burner 14 where it rolls on the lining of the burner. Excess air is supplied to the burner at feeder outlet 15 under conditions to promote combustion of the residuum within the burner and to maintain the temperature below the point at which the burner lining would fuse with the partially burned bitumen. Air is supplied to the burner through air box 33 by means of forced air fan 18. The residuum is introduced into the burner by conveying means 16 which together with the main burner shell 14, is powered by driving gear 17. The hot gases pass from the burner to a boiler fire box and thence around tubes 19 and are withdrawn by means of flue gas duct 21. Tubes 19 comprise an integral part of boiler 20. The residuum is coked and largely burned in burner 14. The incompletely burned particles pass from the burner with the combustion gases into the boiler fire box where they are subjected to roasting, further oxidizing the carbon content and increasing the vanadium percentage content. Under the conditions of the operation, the flue gases removed by flue gas duct 21 contain considerable vanadium dust. This dust is preferably removed from the flue gases by means of a circulated liquid and the dissolved vanadium compound precipitated from the liquid. If this operation be employed, the flue gases are passed to stack 22 through flue gas scrubber 23 wherein the flue gases are contacted with a washing liquid which is introduced by means of line 24. The washing liquid preferably comprises water. The water containing vanadium bearing dust suspended or dissolved therein, is removed by means of line 25 and passed to settling zone 26 in which zone the dust is separated from the water and removed by means of line 27, while the washing liquid is recirculated to scrubber 23 by means of pump 34. A part of the vanadium remains with the dust and may be recovered therefrom in subsequent operations. A part of the vanadium is also dissolved in the wash water. The concentration of vanadium may be increased by the water recirculation. A portion of the water is withdrawn from settling zone 26 by means of line 28 and passed to vanadium precipitating zone 29 wherein a reagent is added and the vanadium compound precipitated from the water. The vanadium compound is removed from zone 29 by means of line 20, while the water is removed by means of line 31. Additional water sufficient to make up for the water withdrawn by means of line 28 is supplied to the system by means of line 32.

The process of the present invention may be widely varied. The invention is essentially directed to a method for recovering vanadium from petroleum oils by utilizing a solid or semi-solid petroleum oil fraction. The invention essentially comprises burning the segregated solid or semi-solid fraction under conditions to produce an ash product having sufficiently high vanadium con-

centration from which it is possible to recover efficiently the same, and in which process vanadium loss as vanadium dust in the flue gases is substantially entirely prevented.

Although the operation may be adapted for the segregation and recovery of vanadium from any petroleum oil containing it, it is particularly adapted for the removal of vanadium from asphaltic type crudes such as Lake Venezuela crudes. The fraction segregated from the crude oil preferably comprises high softening point bitumen bottoms, such as those having softening points in the range above 300° F., preferably those having softening points in the range from about 350° F. to 425° F., as determined by test D36–26 A. S. T. M. method, "Softening Point of Bituminous Materials—Ring and Ball Method."

A particularly desirable operation comprises segregating brittle bitumen representing from about 10% to 20% bottoms of Venezuelan crudes, which pitches have softening points in the range from about 250° F. to 450° F., and which preferably have softening points of about 350° F. The bituminous product segregated may be burned in the solid form either as lumps or granules in a special burner such as the one described or as powder from a modified coal pulverizer, through a water-cooled burner nozzle, and the product of initial combustion roasted to produce ash high in vanadium oxide content.

When the coke particles produced in the initial combustion of bitumen are first introduced from the burner into the boiler fire box, they contain an excessive amount of carbon. However, in accordance with the present process the coke particles are allowed to accumulate on the floor of the fire box and excess air is supplied for their oxidation. Under these conditions the coke particles will be roasted and further decarbonized. When the solid petroleum material is discharged into the burner or kiln the volatile components are disengaged almost instantly thereby contributing their heat to the burner or kiln. The coke resulting from this initial combustion is difficult to burn but is eventually oxidized in accordance with the present process to ash by being retained in the furnace for an appreciable period of time at elevated temperatures. In the roasting process the coke loses the major portion of its carbon content, resulting in an ash having a relatively high concentration of vanadium.

Vanadium bearing brittle bitumen or petroleum pitch may be introduced into the fire box by blowing means or by a chute or by employing mechanical means. In practicing the present invention, it is desirable to water jacket the feed nozzle or burner in order to prevent the feed stock from melting therein. The larger particles of coke produced in the initial flash combustion are preferentially disposed in the furnace so as to permit continued oxidation under the influence of a high furnace temperature and excess air either in the roasting zone or combustion zone. If this former operation be employed, the auxiliary air is supplied preferably through the floor on which the coke is roasting, if the latter operation be employed, the auxiliary air is supplied at the burner inlet. The use of both sources of air may be desirable. By operating in this manner a floor dust having a high concentration of vanadium is produced, which dust is recovered as hereinafter described from the fire box and from the flue gases which contain an appreciable concentration of the same. The term "excess air" used herein means a quantity of air greater than that necessary to effect complete combustion of coke or other carbonaceous materials contained in the oil fraction or residue treated.

I have found that Venezuelan crude oil contains about 0.03% of vanadium and that the bitumen produced by vacuum distillation of the reduced crude or uncracked crude contains about 0.13% of vanadium. By burning this bitumen in a hot furnace or kiln as described, the bitumen loses 50% to 80% of its weight almost instantaneously and the remaining coke is very difficult to burn. I have found that such a coke representing about 46% of the bitumen requires roasting of about one hour at a temperature of 1500° F. in the presence of a considerable excess of air, in order to oxidize the ash. The ash produced as described contains from about 10% to 30% of vanadium oxide.

The fly ash containing an appreciable amount of vanadium may be recovered in any satisfactory manner, as for example, by Cottrell precipitator or by means of a cyclone dust separator. It is, however, preferred to recover the fly ash by washing the flue gases, preferably with a washing solvent comprising water. In accordance with a preferred operation, the water is recirculated to contact additional portions of the flue gases in order to increase the concentration therein of dissolved vanadium compounds since more water is needed to remove dust from flue gas than is required to dissolve all the available vanadium compounds therein. The dissolved vanadium compounds may be recovered by any suitable method, such as by precipitation, utilizing a reagent as for example lead chloride or an equivalent reagent. One distinct advantage of an operation of this character is that the fine particles of fly ash removed by the water solvent are richer in vanadium than the coarser particles and the vanadium is thus more readily recovered.

Vanadium pentoxide is soluble in cold water to the extent of 0.8 part by weight per 100 parts. In order to secure this concentration it is desirable to recirculate the water from about five to twenty-five times, employing a usual rate of water supply as, for example, 15 to 25 pounds of water per 1,000 cubic feet of flue gas. The solvent is removed from the scrubber and passed to the settler wherein the fly ash is deposited and where a clarified liquid is separated and recirculated to the scrubber. A portion of the clarified liquid is withdrawn continuously and treated for vanadium recovery, usually by treating with a solvent such as lead chloride or by cooling, and the like.

In order to illustrate the invention further, the following examples are given which should not be construed as limiting the same in any manner whatsoever:

Example 1

Lump bitumen representing about 18% bottoms of a Venezuelan crude and having a softening point of about 350° F. was fed into a horizontal rotary kiln which discharged into a boiler setting. It was found that the coke formed by the initial flash combustion was in the form of light flakes containing 1.5% vanadium oxide. These flakes were further oxidized in the kiln before being blown out onto the floor of the boiler. The floor dust and the fly ash were oxidized under these conditions to vanadium oxide content of 7.5% to 14.5% respectively. In the same equipment operated with less excess air, the kiln temperatures rose to about 2200° F., which caused

the coke to fuse and drop in strings from the top of the rotating kiln. These strings contained 4.5% vanadium oxide.

Example 2

In an operation in which lump bitumen of the character described was fed into a hammer type pulverizer and then discharged into a boiler setting through a water-cooled burner, it was found that the floor dust averaged about 5.0% vanadium oxide and the fly ash averaged about 8% vanadium oxide.

The vanadium-containing ash may be handled by any suitable method. For example, the ash or flue dust may be mixed with a suitable fluxing reagent, such as alkali and alkaline earth metal carbonates, and roasted in a reverberatory furnace. A preferred fluxing agent comprises sodium carbonate. The slag thus formed is leached with water, after which the water solution may be treated chemically for removal of vanadium or may be evaporated and the residue so obtained reduced to ferro vanadium. The "Thermite process" may also be used as a suitable means of converting the vanadium to ferro vanadium.

The vanadium may be segregated from the concentrated ash by treating with fuming hydrochloric acid in the presence of ethyl alcohol. The solution thus obtained is filtered, in which case metallic compounds insoluble in the above treatment will remain as a residue, and the filtrate evaporated with excess acid. The residue so obtained may be treated with an alkali metal hydroxide solution such as a sodium hydroxide solution, the vanadium contained therein oxidized with a suitable oxidizing agent such as chlorine, after which ammonium vanadate is precipitated by the addition of ammonium chloride to the solution. This precipitate represents a rather pure material, and if desired may be converted to vanadium pentoxide by suitable ignition. The vanadium concentrate so obtained may be employed directly in processing of iron while making various steels. The ash obtained by the present operation, particularly when utilizing a Venezuelan crude oil, also contains various other metallic elements such as nickel, aluminum, and iron. Thus, the vanadium concentrate may be added directly to operations involved in the metallurgy of iron, particularly the iron ore going to blast furnaces, in order to produce directly a vanadium iron alloy.

The vanadium may also be recovered from the ash by chemical treatment involving an initial treatment with nitric acid. The solution so obtained is freed of foreign elements such as lead by a suitable means known to the art as, for example, with aqueous and ammonium sulfide. The precipitate formed at this point is removed and the filtrate acidified, whereupon a precipitate of vanadium sulfide forms which is separated. Further purification or processing of the vanadium so obtained may be followed. The product may be roasted, followed by an alkali fusion so that the vanadium salt will be formed. The sodium vanadate so obtained is crystallized out of solution as ammonium vanadate by the addition of ammonium chloride. The vanadate may be heated to produce vanadium pentoxide.

I claim:

1. Process for the recovery of vanadium from peroleum oils, which comprises treating the petroleum oil in a manner to segregate a relatively high boiling fraction of semi-solid to solid material, burning said high boiling fraction in the presence of sufficient air to burn a major proportion of the combustible materials in said high boiling fraction, segregating the resulting ash and recovering the vanadium therefrom.

2. Process as defined by claim 1, in which said relatively high boiling fraction has a softening point in the range from about 350° F. to 425° F.

3. Process as defined by claim 1, in which said relatively high boiling fraction comprises from about 10% to 20% bottoms of asphaltic type crudes and in which said product is oxidized at a temperature of about 1500° F. to 2000° F. in the presence of excess air.

4. Process as defined by claim 1, in which said segregated petroleum oil fraction is subjected to oxidation for a period of about one hour at a temperature of 1500° F. to 2000° F. in the presence of considerable excess air.

5. Process for the recovery of vanadium from petroleum oils containing the same, which comprises treating the petroleum oil in a manner to segregate a bitumen fraction having a softening point in the range from about 250° F. to 450° F., cooling said bitumen fraction and granulating the same, subjecting the granulated bitumen fraction to oxidizing conditions at elevated temperatures in the presence of excess air sufficient to oxidize substantially all of the carbonaceous content of said bitumen fraction, removing the resulting ash and recovering the vanadium therefrom.

6. Process as defined by claim 5, in which said bitumen fraction has a softening point of about 350° F. and in which said fraction is subjected to oxidation at a temperature of 1500° F. to 2000° F. for a period of about one hour.

7. Process for the segregation of vanadium from petroleum oils containing the same, which comprises treating said petroleum oil in a manner to segregate a semi-solid to solid bitumen fraction having a softening point in the range from about 250° F. to 450° F., burning said bitumen fraction at elevated temperatures in the presence of excess air sufficient to oxidize substantially all of the carbonaceous content of said bitumen fraction, removing the carboniferous ash and recovering the vanadium therefrom, removing the gases from the oxidation zone, and treating the same to remove vanadium compounds therefrom.

8. Process as defined by claim 7, in which said vanadium compounds are removed from said gases by treating with a solvent comprising water.

9. Process as defined by claim 7, in which said vanadium compounds are removed from the gases by treating with a washing solvent comprising water, which solvent is subsequently treated to precipitate vanadium compounds therefrom.

10. A process for the recovery of vanadium from petroleum oils containing the same, which comprises treating the petroleum oil in a manner to segregate a relatively high boiling fraction of semi-solid to solid material, subjecting said high boiling fraction to combustion in at least two stages to burn a major proportion of the combustible materials contained in said high boiling fraction, separating the resultant ash and recovering the vanadium therefrom.

11. A process for the recovery of vanadium from petroleum oils containing the same, which comprises treating the petroleum oil in a manner to segregate a semi-solid to solid bitumen fraction having a softening point in the range from about 250° F. to about 450° F., cooling said bitumen fraction and finely subdividing the same,

subjecting the finely subdivided bitumen to combustion in at least two stages in the presence of excess air to burn a major proportion of the combustible materials contained in said bitumen fraction, separating the resultant ash and recovering vanadium therefrom.

12. A process for the recovery of vanadium from petroleum oils containing the same, which comprises treating the petroleum oils in a manner to segregate a bitumen fraction having a softening point in the range from about 250° F. to 450° F., cooling said bitumen fraction and finely subdividing the same, subjecting the finely subdivided bitumen to combustion with an excess of air, collecting the incompletely burned particles produced in this combustion in a heated zone, supplying excess air thereto, roasting and decarbonizing the same, separating the ash formed and recovering the vanadium.

13. A process for the recovery of vanadium from petroleum oils containing the same, which comprises treating the petroleum oils in a manner to segregate a bitumen fraction having a softening point in the range from about 250° F. to 450° F., cooling said bitumen fraction and finely subdividing the same, subjecting the finely subdivided bitumen to combustion with an excess of air, collecting the incompletely burned particles produced in this combustion in a heated zone, supplying excess air thereto, roasting and decarbonizing the same, passing the combustion gases and entrained ash particles through a scrubber, washing the said gases with a liquid capable of dissolving vanadium pentoxide and recovering the vanadium therefrom.

14. A process for the recovery of vanadium from petroleum oils containing the same, which comprises treating the petroleum oils in a manner to segregate a bitumen fraction having a softening point in the range from about 250° F. to 450° F., cooling said bitumen fraction and finely subdividing the same, subjecting the finely subdivided bitumen to combustion with an excess of air, collecting the incompletely burned particles produced in this combustion in a heated zone, supplying excess air thereto, roasting and decarbonizing the same, passing the combustion gases and entrained ash particles through a scrubber, washing the said gases with a liquid capable of dissolving vanadium pentoxide, recirculating the washing liquid through the scrubber in order to increase the concentration of vanadium compounds dissolved therein, and recovering the vanadium therefrom.

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