

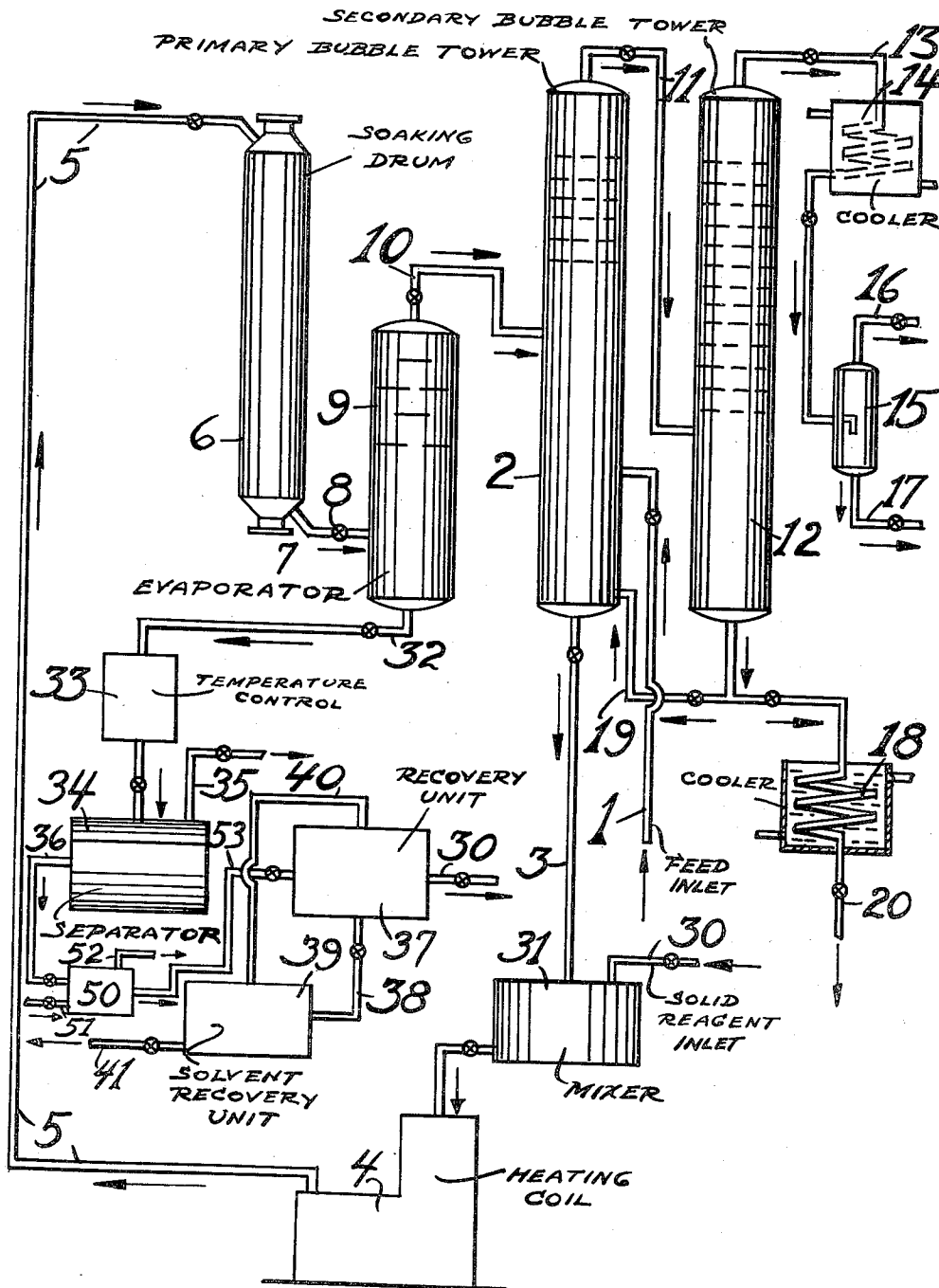
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RECOVERY OF VANADIUM AND NICKEL FROM PETROLEUM

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RECOVERY OF VANADIUM AND NICKEL FROM PETROLEUM

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The present invention is concerned with the recovery of valuable metallic constituents from mineral oils. The invention is more particularly concerned with the recovery of metallic constituents of the class consisting of molybdenum, vanadium, nickel and zinc, from petroleum oils containing the same. In accordance with the present process, these metallic constituents are substantially completely removed and recovered from oils containing the same by contacting the oils with a solid reagent selected from the class of substance having the ability to react therewith.

It is known in the art that mineral oils, particularly certain petroleum oils contain appreciable quantities of vanadium, molybdenum, nickel and zinc. These materials are very desirable and various processes have been suggested for removing and recovering the same. For example, one method employed for recovering these metallic constituents is to reduce the petroleum oil to an ash and then to separate the vanadium compounds by leaching the ash with various leaching solvents having a preferential solubility for the metallic compounds. This process has the disadvantage that the value of the petroleum oil as a fuel is destroyed, which materially increases the cost of recovering these metallic constituents. Various other processes have also been proposed which, due to one fact or another, are not particularly desirable.

I have now discovered a process by which metallic compounds selected from the class consisting of molybdenum, vanadium, nickel and zinc, particularly vanadium, may be efficiently and economically recovered. My process preferably involves utilizing the sensible heat and the existing pressure of current refining operations, and is especially adapted to be used in conjunction with an operation in which a petroleum oil is subjected to elevated temperature and pressure conditions adapted to produce relatively lower and relatively higher boiling constituents. In accordance with my process, these metallic constituents of the petroleum oil, under the temperature and pressure conditions existing in the refining operation, react with the solid reagent of the present invention, and are readily removed from the petroleum oil and recovered from the solid reagent.

The process of my invention may be readily understood by reference to the attached drawing illustrating modifications of the same. For purposes of description, it is assumed that the metallic constituent containing feed oil is a petroleum oil boiling in the reduced crude boiling range. My process as illustrated in the drawing

is employed in conjunction with a typical reduced crude cracking operation. In this operation the feed oil boiling in the range above about 500 to 700° F. is introduced by means of feed line 1 into the lower section of primary bubble tower 2. The feed oil, along with recycle oil, is withdrawn from the bottom of primary bubble tower 2 by means of line 3 and introduced into heating coil or furnace 4 which is so designed as to secure optimum heat transfer rates and to raise the oil to the desired temperature and pressure. Prior to introducing the oil into heating coil 4, it is mixed with an amount of solid reagent which is introduced by means of line 30. The solid reagent is selected from the class of materials which will react with the desirable metallic constituents and which will not have any substantial effect on the cracking rates or conditions or the yields of the cracking operation.

For purposes of description it is assumed that the solid reagent is a naturally occurring hydrated sodium aluminum silicate of the zeolite type. Complete mixing is secured by passing the zeolite and oil through mixer 31. The total feed along with the zeolite is passed through the tubes in the radiant and convection sections of furnace 4 in which the oil is raised to the desired cracking temperature. The heated oil is withdrawn from furnace 4 by means of line 5 and passed into soaking drum or reaction chamber 6 which, for the purposes of illustration, is assumed to be a down-flow type soaking drum. Reaction drum 6 is designed to permit maintaining the oil for an additional optimum time period under cracking conditions. The oil, along with the zeolite, is withdrawn from reaction drum 6 by means of line 7 and passed through pressure release valve 8. The cracked products pass into evaporator 9 from the bottom of which tar or fuel oil of the desired gravity is removed. The flashed vapors pass overhead from evaporator 9 through line 10 and are introduced into the middle section of primary bubble tower 2. Cycle stock accumulates in the bottom of primary bubble tower 2 which is recycled with the fresh feed as described. Vapors pass overhead from bubble tower 2 by means of vapor line 11 and are introduced into a secondary bubble tower 12. The temperature maintained at the bottom of primary bubble tower 2 is usually adapted to secure the desired end point on the heating oil fraction which is withdrawn from the bottom of secondary bubble tower 12. The temperature at the top of secondary bubble tower 12 is controlled to produce an overhead distillate of the desired end point. This distillate is removed

by means of line 13, condensed in cooler 14, and then passed into distillate drum 15. Uncondensed gases are removed from the top of distillate drum 15 by means of a line 16 and handled in any manner desirable, usually by passing to a high pressure burning line. The condensed distillate which usually comprises constituents boiling in the motor fuel boiling range is removed from distillate drum 15 by means of line 17, further stabilized and refined, and then blended to produce finished motor fuels. Higher boiling petroleum constituents, usually boiling in the heating oil boiling range, are removed from the bottom of secondary bubble tower 12, passed through cooler 18, and withdrawn from the system by means of line 20.

Tar or heavy fuel oil containing the zeolite and the metallic constituents is removed from the bottom of evaporator 9 by means of line 32 and passed through temperature control unit 33, in which it is possible to either raise or lower the temperature of the tar or heavy fuel oil fraction to the desired degree. The heavy oil fraction is withdrawn from the temperature control unit 33 and passed into separator 34 which may comprise any suitable number of units of any desired design, in which the zeolite is separated from the heavy fuel oil or tar fraction. The tar or fuel oil fraction is withdrawn from the system by means of line 35 and handled in any manner desired. The zeolite containing the metallic constituents is withdrawn from separator 34 which may comprise a metallic screen filter by means of line 36 and handled to remove and recover the metallic constituents from the zeolite by suitable means. This is preferably accomplished by passing the zeolite to a solvent washing unit 50 in which the tarry oil fractions are removed from the zeolite by washing with a solvent which is introduced by means of line 51 and withdrawn by means of line 52. The zeolite substantially free of oily constituents is withdrawn from washing unit 50 by means of line 53 and handled in a manner to remove and recover the metallic constituents from the zeolite. This is preferably accomplished by treating the zeolite with a solvent having the ability to partially dissolve the metallic constituents from the zeolite. Solvents of this class are for example various diluted solutions of mineral acids as for example sulfuric, hydrochloric and nitric acid. The zeolite, free of recovered metallic constituents, is removed from recovery unit 37 by means of line 38, regenerated, and recycled to the system. Following the acid treatment, the reagent becomes a hydrogen zeolite and it is treated with a brine such as a sodium chloride brine to regenerate the zeolite and form the sodium zeolite. Although the step of regenerating the reagent may be employed in applicant's novel process and forms a valuable adjunct thereto, it is not per se novel. The solution of recovered metallic constituents is removed from unit 37 by means of line 39 and passed to solvent recovery unit 39 in which the solutions are handled in a manner to recover the metallic constituents. The solvent, as desired, may be recycled to the recovery unit by means of line 40, while the recovered metallic constituents may be withdrawn from the system by means of line 41.

The process of the invention may be widely varied. In general the invention is concerned with a process adapted to the recovery of metallic constituents of the class consisting of molybdenum, vanadium, nickel and zinc from mineral oils, particularly from petroleum oils containing

the same. Although my process may be employed in the recovery of these constituents from mineral oils under wide varying conditions, it is especially adapted to be employed in conjunction with normal refining operations. I have found that especially desirable results are secured when employing my method in conjunction with conventional cracking operations for the recovery of vanadium from petroleum oils.

The solid reagent employed is selected from the class of substances having the ability to react with these metallic constituents and is further characterized in that the reagent will not affect the normal refining operation. Suitable solid reagents are for example (1) mixtures of sodium carbonate and various clays such as kaolin, (2) zirconium oxide, (3) kaolin alumina mixtures, (4) diatomaceous earths, (5) alkali metal salts such as sodium carbonate and potassium carbonate, and (6) the salts of iron and lead which form lead vanadates and ferric vanadates and the like. A particularly desirable material comprises molten sulfur which precipitates out of the tar along with the vanadium upon cooling. However, in general the preferred solid reagents are selected from the class of alkali metal aluminum silicates of the zeolite type, especially the naturally occurring hydrated alkali metal aluminum silicates, as for example a naturally occurring hydrated sodium aluminum silicate having the formula $\text{NaH}_2\text{AlSiO}_4$.

The temperatures and pressures will be a function of the characteristics of the particular feed oil, and will also depend upon the concentration of the metallic compounds present as well as upon the type of reagent employed. When utilizing a zeolite, the temperature and pressure conditions are generally in the range at which substantially no decomposition of the oil occurs due to the effect of the zeolite. In general the temperatures are in the range from about 250° to 800° F., but higher temperatures in the range above about 1000° F., are preferred and the pressures vary from atmospheric to oil cracking pressures. It is preferred that the pressures be in the range from about 750 to 1000 lbs./sq. in.

The metallic constituent may be recovered from the product resulting from the reaction with the reagent by processes essentially involved in solvent treatment or roasting. For example, if sulfur be used as the reagent, the vanadium may be recovered from the sulfide by roasting to produce the vanadium oxide and then reduced to substantially pure vanadium by a selective furnace roasting reaction. If zeolite be employed, the vanadium is extracted by solvent treating the zeolite with a strong mineral acid as for example a strong solution of hydrochloric or sulfuric acid. The vanadium is precipitated from the acid solution preferably as ammonium vanadate by evaporating the acid solution with an excess of ammonium chloride. The ammonium vanadate is then roasted to produce the oxide which may be reduced by means of an electric furnace. The solid absorbent containing the recovered metallic constituents may if desired be withdrawn directly from the system. However it is preferred to employ conventional means for removal and recovery of these constituents and to recycle the solid reagent.

A modification of the present invention is to introduce the solid reagent into the feed oil of a cracking unit in a finely divided or powdered form. The reagent at the high temperatures and at the pressures existing in the unit, reacts with

the vanadium present. Upon withdrawal of the tar, the reagent is allowed to settle while the tar is still hot and limpid. The reagent is removed and again employed for the recovery of vanadium in the manner described. The solvent employed for removing the occluded tarry oil fractions from the solid absorbent containing the vanadium after separation from the tarry fraction is preferably a relatively low boiling petroleum oil fraction. A particularly desirable solvent comprises a petroleum oil fraction boiling in the range from about 300° F. to 450° F. Under certain operations it may be desirable to remove the tarry fractions from the absorbent by burning.

In order to more fully illustrate the invention, the following examples are given which should not be construed to restrict the same in any manner whatsoever.

Example 1

A feed oil representing the highest 8% boiling fraction of a Lake Venezuela crude oil was passed over pumice at a temperature of about 900° F., at a velocity of about 23 feet per second. Analysis of the treated oil after 4800 units were treated indicated that substantially complete removal of the vanadium from the oil was secured and that the vanadium content of the pumice was about 0.24%.

Example 2

A reduced Venezuela Lagunillas crude was passed over a mixture comprising 50% sodium carbonate and 50% kaolin at a temperature of about 780° F. to 820° F. and at atmospheric pressure. The feed rate employed was 1.2 volumes of oil per volume of catalyst per hour. At the end of a four hour period, it was found that the solid reagent contained 0.29% of vanadium oxide.

The process of the present invention is not to be limited by any theory or mode of operation but only by the following claims in which it is desired to claim all novelty insofar as the prior art permits.

I claim:

1. Process for the removal and recovery of metallic constituents of the class consisting of molybdenum, vanadium, nickel and zinc from petroleum oils containing the same, and for the production of relatively higher and relatively lower boiling petroleum oil constituents by cracking, which comprises mixing the said petroleum oil with a solid reagent selected from the class of naturally occurring hydrated alkali metal aluminum silicates of the zeolite type, passing the feed oil through heating means adapted to raise the

oil to the desired cracking temperature and pressure level, maintaining the feed oil under the desired conditions for the optimum time period, then passing the same through a pressure release valve into an evaporator adapted to concentrate a relatively small quantity of the relatively higher boiling constituents, removing the relatively higher boiling constituents along with the solid reagent containing the desired metallic constituents from the bottom of said evaporator, physically separating the relatively higher boiling constituents from the solid reagent containing the metallic constituents, and recovering the metallic constituents therefrom.

2. Process for the separation and recovery of vanadium from petroleum oils containing the same and for the production of relatively higher and relatively lower boiling petroleum oil constituents which comprises mixing the feed petroleum oil with a solid reagent selected from the class of alkali metal aluminum silicates of the zeolite type, which will react with the vanadium and which will not substantially affect the refining operation, passing the feed oil through heating means adapted to raise the oil to the desired cracking temperature and pressure level, maintaining the feed oil under the desired conditions for the optimum time period, then passing the oil through a pressure release valve into an evaporator adapted to concentrate a relatively small quantity of the relatively higher boiling constituents, removing the relatively higher boiling constituents along with the zeolite containing the vanadium, and recovering the vanadium therefrom.

3. Process for the separation and recovery of vanadium from mineral oils containing the same which comprises contacting the feed mineral oil with an alkali metal aluminum silicate of the zeolite type at an elevated temperature and pressure, which deposits a coating of relatively high boiling mineral oil constituents upon the zeolite, separating the zeolite from the mineral oil, treating the zeolite with a relatively low boiling petroleum oil solvent to remove relatively high boiling mineral oil constituents therefrom, separating the zeolite containing the vanadium and recovering the vanadium therefrom.

4. A process according to claim 3 wherein the separated zeolite type reagent is regenerated and recycled to the oil treating step for removal of additional amounts of vanadium from fresh mineral oils.

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