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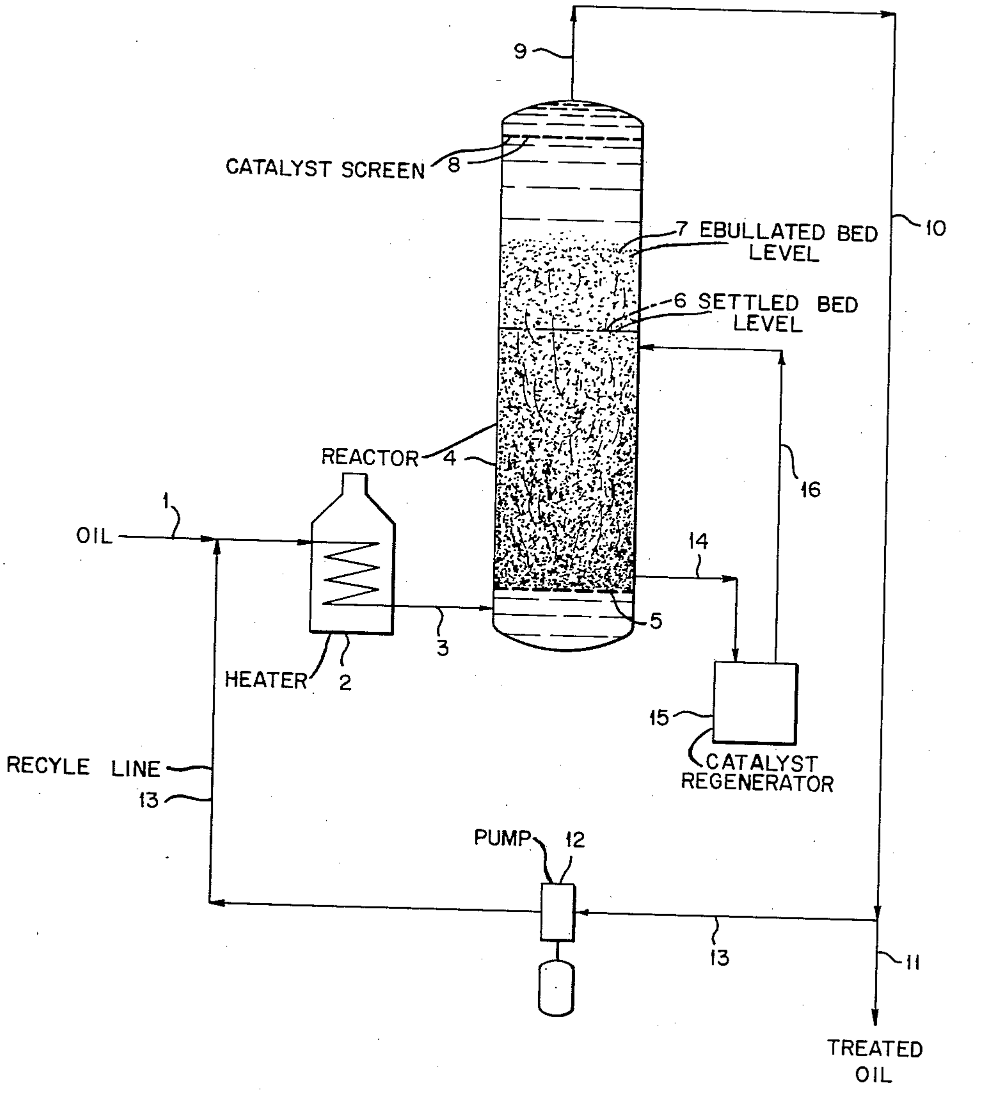

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DEMINERALIZATION OF OILS

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This invention relates to an improved process for the demineralization of hydrocarbon oils.

It has been known for some time that hydrocarbon oils often contain significant quantities of metallic impurities, e.g., vanadium, nickel, sodium, iron, copper and zinc. These impurities may be in the form of insoluble compounds suspended in the oil or oil-soluble metallo-organic compounds, e.g., porphyrin complexes. Compounds of the latter type have been found to be extremely stable and are often also fairly volatile so that they are present not only in residual oils but in distillate oils as well.

The presence of these metallic impurities in hydrocarbon oils is very undesirable. If the oil is subjected to a catalytic conversion process, e.g., catalytic hydrogenation or catalytic cracking, the metallo-organic compounds tend to form a layer of ash on the surfaces of the catalyst, thus blocking or otherwise adversely affecting the activity of the catalyst and often permanently poisoning it in terms of both activity and selectivity. This is quite different from the ordinary inactivation of the catalyst by coke formation which is taken care of by frequent regeneration, i.e., burning off of the carbonaceous deposits formed during the reaction. If the oil is used as a fuel in an internal combustion engine, the metallic impurities in the oil may lead to a troublesome formation of solid metal-containing deposits in the combustion chamber of the engine, thus causing such engine to function in an inefficient manner. If the oil is used for lubricating purposes, solid particles tend to be formed from the oil-soluble metallo-organic impurities as a result of the heat and pressure caused by the movement of the surfaces being lubricated and such solid particles are injurious to the moving surfaces. While metallic impurities present in an oil in the form of suspended solid particles may be removed by relatively simple physical means like filtration, oil-soluble metallo-organic compounds present a more difficult problem of elimination because of their stability, volatility and solubility.

It is an object of this invention to provide an improved process of removing oil-soluble metallo-organic impurities from hydrocarbon oils. It is a further object to effect the removal of oil-soluble metallo-organic impurities from a hydrocarbon oil by contacting the oil with particulate contact material on the surfaces of which the impurities deposit.

In accordance with this invention, a hydrocarbon oil containing at least one oil-soluble metallo-organic impurity is passed upwardly through a demineralization zone which contains a mass of particulate contact material at a liquid velocity which is sufficiently high to cause the particles of contact material to move in random motion with respect to each other but insufficient to cause the particles to be carried out of the demineralization zone. The degree of random motion is such as to cause the gross volume of the particles in the demineralization zone to be expanded at least 10% over that of the settled volume of the contact material. Particulate solids in such a state of random motion are referred to as "ebullated" and the technique of ebullation is explained in copending application Serial No. 743,304, filed June 20, 1958, by E. S. Johanson. On contacting the ebullated solids, the oil-soluble metallo-organic impurities are substantially deposited on the solids or converted to solid particles which become entrained in the oil. The particles of contact material in the ebullated state rub against each other and the walls of the demineralization zone so that part of the metallic impurities deposited on the surfaces of the ebullated solids in an insolubilized condition and other deposits, e.g., of a carbonaceous or hydrocarbonaceous nature, tend to be rubbed off the ebullated solids and to be carried with the oil as entrained fine particles. Such entrained insoluble metal-containing particles exert a much less harmful effect on the catalyst if the oil is subsequently put through a catalytic conversion process than do the metallic impurities in the form of oil-soluble metallo-organic compounds present in the oil before demineralization by the process of this invention. If the oil is intended for a use which makes it desirable to remove entrained particles, the oil may be passed through a centrifuge or filter to separate out the solid particles.

An advantage of the demineralization process of this invention is that the spaces between the particles or free volume of the ebullated mass is to a large extent determined by the velocity of oil flowing through the demineralizer, i.e., the greater the velocity, the larger the free volume. This factor together with the slower build-up of deposits when the contact material is ebullated causes the pressure drop across the demineralizer to be initially small and to remain small as the demineralization process proceeds. This is substantially different from a conventional fixed bed of contact material wherein because the particles are substantially contiguous to one another the pressure drop of the oil passed therethrough is initially fairly large and rapidly becomes larger as the deposits on the surfaces of the contact material and the walls of the demineralizer build-up. Thus, the power consumed in pumping the oil through a demineralizer containing ebullated solids in much less than if a conventional fixed bed of contact material were used and a fixed bed could not be operated for more than a few days when it would become plugged with deposits.

The velocity of oil which is necessary in any process to ebullate the particulate contact material in the demineralizer depends among other things on the density, size and shape of the particles of contact material and the density and viscosity of the oil under the conditions of demineralization. However, it is a relatively simple matter to operate any particular process so as to cause the mass of selected contact material to become ebullated and to calculate the percent expansion of the ebullated mass after observing its upper level of ebullation through a glass window in the vessel or by other means such as oil samples drawn from the vessel at various levels. In most processes carried out in accordance with this invention, the contact particles will be approximately of a size passing through ¼ inch mesh openings but retained by $\frac{1}{32}$ inch mesh openings (i.e., between about 3 and 20 mesh screens of the Tyler scale), the gross density of the stationary mass of contact material between about 25 and 200 pounds per cubic foot, the flow rate of the oil between about 20 and 120 gallons per minute per square foot of horizontal cross-section of the ebullated mass, and the expanded volume of the ebullated mass not more than about double the volume of the settled mass. In certain cases, oil flow rates as low as 5 and as high as 500 gallons per minute per square foot of horizontal cross-section of the ebullated mass may be used. Similarly, the expanded volume of the ebullated mass may be several times the volume of the settled mass but expanding the settled mass by ebullation to a volume more than three times its original volume is rarely justified on technical or economic grounds.

The velocity of oil necessary to ebullate the mass of contact material may be obtained with once-through oil flow, using a demineralizer of sufficient height to provide the oil with enough residence time and contact with the ebullated solids to effect the desired conversion and elimination of oil-soluble impurities. Alternatively, only a moderately high demineralizer may be used when employing an oil recycle stream. There is no theoretical maximum to the size of the recycle stream, i.e., the volume ratio of recycled oil to fresh feed may be as high as 20 or 30 to 1. The residence time of the oil in the demineralizer required in any particular process will depend on such known factors as the nature and quantity of oil-soluble metallic impurities present, the temperature in the demineralization zone and the selected contact material. Generally, the desired amount of demineralization of an oil is achieved at a space velocity in the range of about 0.5 to 5 volumes of oil per hour per volume of ebullated mass; the preferred range of space velocities is 1 to 3 oil volumes per hour per ebullated mass vloume.

The particulate contact material used in the demineralizer may be any solid which will withstand the operating conditions, e.g., bauxite, alumina, sand, coke, beryl, silicon carbide, magnesia and iron ore. In general, the physical and chemical structure of these solids is not critical and they are considerably less expensive when compared with the usual catalysts employed in the cracking and hydrogenation of hydrocarbon oils. In fact, the solids in the demineralizer may be spent or poisoned catalyst from such a conversion process. While such solids are no longer effective for catalyzing the particular hydrocarbon conversion for which they were manufactured, they are usually effective for the deposition or insolubilization of oil-soluble metallic impurities.

The temperature and pressure at which the demineralization process is carried out may vary within wide limits, e.g., 600 to 1000° F. and 0 to 5000 p.s.i.g. (pounds per square inch gage), depending on the nature and purpose of the particular process. While the oil being treated is largely in the liquid phase, the presence of vapors due to the volatilization of the lighter components of the oil under the conditions of demineralization does not adversely affect the results. In some cases, it is found that the introduction of hydrogen into the demineralizer assists the removal or destruction of oil-soluble metallic impurities.

The process may be carried out with all of the contact material remaining in the demineralizer and with periodic interruptions of the process for substituting a fresh mass of contact material when the deposits on the ebullated solids have built up to a point where the contact material is insufficiently effective against the oil-soluble metallic impurities. This is a satisfactory method of operation when the quantity of oil-soluble metallic impurities in the oil is relatively small. However, when the quantity of oil-soluble impurities in the oil is relatively large, it is advantageous to remove contact material substantially continuously from the demineralizer, treat it to remove surface deposits, and then return it to the demineralizer. An apparatus for removing deposits from the contact material is described, for example, in Industrial & Engineering Chemistry 49, 865–8 (1957).

The process of this invention is especially suitable for the treatment of oils which are intended as feed to a catalytic conversion process utilizing a catalyst susceptible to poisoning by metallic impurities. Two of the more important of these conversion processes are catalytic cracking to produce gasoline from heavier oils and catalytic hydrogenation of oils to remove surfur compounds, nitrogen-containing impurities, and gum-forming substances, and when Diesel fuel is involved, to improve the cetane number. An oil may also be catalytically hydrogenated prior to catalytic cracking to improve the gasoline yield When the feed stock to the catalytic conversion process contains a significant amount of oil-soluble metallic impurities, the activity and selectivity of the catalyst will be maintained high for a longer period of time if the oil is first demineralized according to this invention than if the oil is not so pretreated. This is true no matter what the specific nature of the catalytic conversion process is, i.e., whether it involves a fixed, moving, fluidized or ebullated bed of catalyst particles and whether the hydrocarbon oil is in the liquid or vapor phase, since in all cases the contact of oil-soluble metallic impurities with the surfaces of the catalyst tends to poison or inactivate it.

The process of this invention is usually applied to oils boiling substantially above the gasoline boiling range, i.e., gas oils and heavier distillate and residual oils, since it is in these oils that oil-soluble metallic impurities such as porphyrin complexes generally occur. However, it is also feasible to treat lighter oils which through any circumstances contain undesirable oil-soluble metallic impurities.

Reference is now made to the accompanying drawing which diagrammatically shows an embodiment of the invention wherein the contact material is periodically or continuously treated to remove the metallic deposits formed in the deminealization zone.

Charge stock from line **1** is combined with recycle oil from line **13** and passed through heater **2**. The preheated oil is thence transferred by line **3** to the bottom of demineralizer **4** which contains a mass of solid particles of contact material supported on screen or perforated plate **5**. When the process is not in operation, the contact material has a stationary bed level **6**. When, however, the process according to this invention is being carried out, the particles are in constant random motion in the oil flowing up through vessel **4**, the mass of particles expanding so that its upper boundary or upper level of ebullation is at **7**. The volume of demineralizer **4** between perforated plate **5** and upper ebullation level **7** corresponds to the ebullated mass volume previously mentioned in connection with the space velocity of the oil undergoing treatment. Vessel **4** may contain a second screen or perforated plate **8** near its top to prevent stray particles of contact material from leaving demineralizer **4** with the reaction effluent. Screen **8** is near outlet **9** well above upper level of ebullation **7**. The effluent discharging through outlet **9** flows through line **10** and part of it is withdrawn through line **11** as demineralized product. The remainder of the oil is circulated by pump **12** through line **13** for recycling to demineralizer **4** after being combined with fresh feed as aforesaid.

The foregoing description illustrates a process which operates batchwise as far as contact material is concerned. When a relatively small quantity of metallic deposits are formed on the contact particles, the process may be operated in this fashion for a considerable period without interruption. However, when substantial deposits are formed on the contact particles, it is necessary to replace the fouled contact material with fresh or regenerated contact material at fairly frequent intervals or even continuously. In such case, contact material may be periodically or continuously withdrawn from demineralizer **4** through line **14** as a slurry and sent to regeneration plant **15**. There the particles of contact material are separated from the oil and treated to eliminate at least some of the metallic deposits thereon. A simple but effective method of removing metallic deposits from the contact particles involves passing the particles through a rotating drum so that the deposits are abraded off by the collisions of the particles with one another and the inner walls of the drum. Vibrating equipment may also be used to rub off the metallic deposits on the contact particles. Still another alternative involves suspending the particles in a high-velocity gas stream and discharging the stream against a target plate so that the metallic deposits on the particles are shattered by the impact. In all of these techniques for removing deposits from the surfaces of the contact particles, the deposits are converted to a very fine dust readily separable from the relatively coarse particles of contact material. Such separation may be made by screening, elutriation or flotation. Treated particles are then reslurried in oil and sent back to demineralizer **4** by way of line **16**.

As a specific example of the invention, a Venezuelan petroleum residue having an initial boiling point of 680° F., and an ash content in the form of oil-soluble metallo-organic compounds of 49 parts per million, over 80% of which are vanadium compounds, is passed in liquid phase through a mas of alumina of 8 to 12 mesh size in a cylindrical demineralizer maintained at a temperature of 760° F. and pressure of 850 p.s.i.g. A space velocity of 2 volumes of oil per hour per ebullated mass volume is employed.

By recycling 18 volumes of treated oil for each volume of fresh feed, a liquid velocity of about 60 gallons per minute per square foot of horizontal cross section of the demineralizer is maintained with the result that the alumina particles are kept in random motion, the ebullated mass of alumina showing an expansion of about 35% over the volume of the settled mass. The demineralized oil contains only 13 parts per million of ash in the form of oil-soluble metallo-organic compounds.

Where a hydrogen-containing gas is available at relatively low cost, it is advantageous to pass it upwardly through the demineralizer along with the oil undergoing treatment. Hydrogen particularly facilitites the decomposition of oil-soluble vanadium compounds. In general, the demineralizer is preferably operated at a temperature in the range of about 700 to 850° F. and a pressure in the range of about 750 to 3000 p.s.i.g.

Many modifications of the invention will occur to those skilled in the art upon consideration of this disclosure without departing from the spirit or scope thereof. For instance, protective screen **8** in demineralizer **4** of the drawing may be omitted and its function may be duplicated by enlarging the horizontal cross-section of the top portion of demineralizer **4** beginning at a level in the vicinity of the upper level of ebullation **7**. Thus, the oil flow rate up through the top portion of demineralizer **4** will be appreciably decreased with the result that entrained particles from the ebullated mass will tend to drop back thereto. Oil may be recycled internally within demineralizer **4**; in such case, a standpipe with an open top end above upper level of ebullation **7** may be used to pass oil from the top of demineralizer **4** to a pump disposed below screen **5** so that oil discharged by the submerged pump will flow upwardly again through the mass of ebullated solids. In lieu of screen **5** which uniformly distributes the flow of oil to the entire mass of ebullated solids in demineralizer **4**, the bottom of this vessel may be tapered or funnel-shaped so that the oil introduced into the bottom of the funnel will flow up uniformly through the entire ebullated mass. Where the oil tends to form some vapors and gases like ethylene during treatment or when hydrogen is used in the demineralizer, the reaction effluent may be discharged from outlet **9** into a gas-liquid separator so as to eliminate gasiform components from the recycle stream passer through lines **10** and **13**. Recycle line **13** may in many cases be connected to the bottom of vessel **4** rather than to fresh feed line **1**. Accordingly, only such limitations should be imposed on the invention as are set forth in the appended claims.

What is claimed is:

1. A process of removing at least part of the oil soluble metallic impurities present in a hydrocarbon oil, which comprises flowing said oil upwardly through a demineralization zone maintained at a temperature in the range of 600 to 1000° F. and at a pressure not exceeding 5000 p.s.i.g. and containing a fixed mass of particulate contact material the particles of which are in the size range of about 3 to 20 mesh screen, regulating the flow of said oil through said demineralization zone in the range of 20 to 120 gallons per minute per square foot of horizontal cross section of said demineralization zone to expand the settled volume of said contact material at least 10% but insufficient to carry the particulate contact material out of said demineralization zone and to cause random movement of the particles of said contact material, and withdrawing from said demineralization zone oil with a reduced content of oil soluble metallic impurities and substantially free of particles of said contact material.

2. The process of claim 1 wherein a portion of the oil from the top of said demineralization zone is recycled to the bottom thereof.

3. The process of claim 1 wherein contact material is withdrawn from said demineralization zone, the withdrawn contact material is treated to remove at least part of the metallic deposits thereon and the treated contact material is returned to said demineralization zone.

4. The process of claim 1 wherein said demineralization zone is maintained at a temperature in the range of about 700 to 850° F. and a pressure in the range of about 750 to 3000 p.s.i.g.

5. The process of claim 1 wherein said contact material is alumina.

6. The process of claim 1 wherein said contact material is bauxite.

References Cited in the file of this patent

UNITED STATES PATENTS

2,706,167	Harper et al.	Apr. 12, 1955
2,758,060	Porter et al.	Aug. 7, 1956
2,914,458	Harper	Nov. 24, 1959