METHOD FOR REDUCING THE TOTAL ACID NUMBER OF A MIDDLE DISTILLATE OIL

Inventors: Robert A. Plundo, Greensburg; Thomas C. Readal, McCandless Township; James R. Strom, O'Hara Township, all of Pa.

Assignee: Gulf Research and Development Company, Pittsburgh, Pa.

Filed: Feb. 27, 1973

Appl. No.: 336,382

U.S. Cl. 208/216; 208/15; 208/263

Int. Cl. C10g 23/02

Field of Search 208/216, 263, 15, 264

References Cited

UNITED STATES PATENTS

2,717,857 9/1955 Bronson et al. 208/216
2,793,986 5/1957 Lanning 208/264
2,921,023 1/1960 Holm 208/216
2,963,425 12/1960 Hansen 208/216
2,998,381 8/1961 Bushnell 208/216
3,483,119 12/1969 Ehler 208/264

Primary Examiner—Delbert E. Gantz

Assistant Examiner—C. E. Spresser

ABSTRACT

Middle distillate virgin oils, such as straight run furnace oil, jet fuel or kerosene are required to meet many commercial specifications, among which are maximum allowable total sulfur content, maximum allowable mercaptan sulfur content and maximum allowable total acid number. Middle distillates which do not meet commercial specifications in regard to total sulfur content can be hyrodesulfurized for the removal of the portion of the total sulfur required for meeting the commercial requirement. Such hyrodesulfurization requires more severe conditions than do processes for reduction of total acid number or for reduction of mercaptan sulfur content so that under the severe conditions required for hyrodesulfurization, excessive total acid number and excessive mercaptan content are automatically concurrently reduced to commercially acceptable levels. The present invention relates to the hyrodesulfurization of virgin middle distillates which meet commercial specifications in regard to total sulfur content in the absence of prior hyro-treating or any other treatment, but do not meet commercial specifications in regard to total acid number or in regard to mercaptan sulfur content. According to the present invention, the latter middle distillates are not blended with high total sulfur feeds flowing to hyrodesulfurization processes requiring severe conditions to accomplish reduction in total sulfur content, but are hyro-treated separately under relatively more mild catalytic hyro-treating conditions to reduce mercaptan sulfur content or total acid number at hyro-treating severities which are so mild that there is an extremely limited consumption of hydrogen and a very limited removal of total sulfur. The catalyst employed in the mild hyro-treating processes of this invention is a deactivated hyro-treating catalyst from a more severe hyrodesulfurization or other hyro-treating operation which is no longer of viable use in the more severe operation due to numerous cycles of use and regeneration, due to excessive metals deposition thereof, or any other reason.

15 Claims, 8 Drawing Figures
FIG. 1

MERCAPTAN DESULFURIZATION, WEIGHT PERCENT

0 20 40 60 80 100

NON-MERCAPTAN DESULFURIZATION, WEIGHT PERCENT

- ORDOVICIAN FURNACE OIL
- WEST TEXAS KEROSENE

FIG. 2

REDUCTION IN TOTAL ACID NUMBER, PERCENT

0 20 40 60 80 100

NON-MERCAPTAN DESULFURIZATION, WEIGHT PERCENT

- SOUTH LOUISIANA FURNACE OIL
- SOUTH LOUISIANA KEROSENE
**FIG. 3**

Percent reduction in bromine number (olefin content) vs. non-mercaptan desulfurization, weight percent.

- HEAVY FCC NAPHTHA
- WEST TEXAS KEROSENE
- WEST TEXAS FURNACE OIL

**FIG. 4**

Mercaptan sulfur, D1923, weight percent vs. percent reduction in mercaptan sulfur vs. reactor temperature, °F.

- 8.0 LHSV, 100 psig (7 kg/cm²)
- 4.0 LHSV, 100 psig (7 kg/cm²)
- 4.0 LHSV, 200 psig (14 kg/cm²)

Reactors temperatures: 400°, 450°, 500° (204°C, 232°C, 260°C).
FIG. 5A

GAS CIRCULATION RATE OF 85% H₂: SCF/B

FIG. 5B

GAS CIRCULATION RATE OF 85% H₂: SCF/B
FIG. 6

[Graph showing total acid number vs. reactor temperature with two lines representing 4.0 LHSV and 8.0 LHSV]

FIG. 7

[Graph showing total desulfurization, weight percent vs. average reactor temperature with lines for fresh catalyst and catalyst at fifth cycle]
METHOD FOR REDUCING THE TOTAL ACID NUMBER OF A MIDDLE DISTILLATE OIL

This invention relates to a very mild hydrotreatment of virgin middle distillates such as furnace oil, kerosene, jet fuels, light gas oils or diesel oils in order to reduce the total acid number or the mercaptan content of the distillate without greatly reducing the total sulfur content of the oils in the presence of a catalyst which has previously been deactivated in a more severe hydrotreating process. This invention is related to two patent applications filed by the same inventors on even date herewith entitled "Method for Utilizing a Fixed Catalyst Bed in Separate Hydrogenation Processes" and "Method for Reducing the Mercaptan Content of a Middle Distillate Oil" bearing Ser. Nos. 336,384 and 336,383, respectively.

The middle distillates of this invention boil generally above the naphtha range and generally exclude lubricating oils.

Middle distillates which do not meet commercial requirements in regard to total sulfur content, which is about 0.2 weight percent sulfur for fuel oils destined for use as home heating fuel, are commonly hydrodesulfurized under relatively severe conditions in order to reduce the total sulfur content to a level at least as low as the commercial requirement. Such hydrodesulfurization processes generally occur in the presence of a Group VI and Group VIII metal containing catalyst such as cobalt-molybdenum, nickel-cobalt-molybdenum or nickel-tungsten on a non-cracking support such as alumina or silica with a small stabilizing but non-cracking amount of silica which can be, for example, less than 0.5 percent, or less than 1 percent by weight. Common severe hydrodesulfurization conditions include a temperature range between 650° or 675° and 800°F. (between 343° or 357° and 426°C.), a pressure of at least 600 psig (42 kg/cm²) and more generally in the range between 1,000 and 2,000 or 3,000 psig (between 70 and 140 or 210 kg/cm²), a liquid hourly space velocity between about 0.7 and 2 and a hydrogen circulation rate of between about 2,000 and 3,000 standard cubic feet per barrel of hydrogen (36 and 54 standard cubic meters per 100 liters), which hydrogen can be about 75 to 80 percent pure. Hydrogen consumption is commonly about 400 standard cubic feet per barrel (7.2 standard cubic meters per 100 liters) at 1,000 psi (70 kg/cm²) operation or about 500 standard cubic feet per barrel (9 standard cubic meters per 100 liters) at 2,000 psi (140 kg/cm²) operation. These are only examples of severe hydrodesulfurization conditions, and are non-limiting.

In refinery operations utilizing such hydrodesulfurization operations, virgin middle distillates from a multiplicity of crude oil sources are commonly combined for feeding to such high pressure hydrodesulfurizers. The various middle distillates that are combined may individually fail to meet commercial specifications in regard to less than all standards. A middle distillate which fails to meet commercial requirements in regard to total sulfur content must be treated under the severe high pressure desulfurization conditions described above. However, in accordance with the present invention it has been found that a straight run middle distillate which does meet commercial total sulfur requirements in the absence of any prior hydrotreatment but fails to meet commercial total acid number require-

ments and/or commercial mercaptan requirements need not be blended with the high total sulfur fuel but can be treated separately in a different reactor under more mild conditions without employing a fresh catalyst but rather employing a catalyst that has been deactivated in a separate reactor under relatively more severe hydrogenation or hydrodesulfurization conditions to a state that its use is no longer viable in the severe hydrogenation operation.

High total acid numbers in oils are primarily due to the presence of naphthenic acids in the oil. The acid attacks copper and zinc in fuel handling systems. This type of metals pick-up not only induces metal losses in pipelines which affect metal ratios in alloys but also causes instability leading to sludge formation in the oil which can cause the oil to deposit sludge on injectors, float controls and other critical parts. In one known case a high neutralization number diesel oil was found to pick up sufficient zinc from a diesel engine to cause engine shutdown. Harmful effects in equipment due to high copper pick-up with employing a high total acid number oil have also been experienced. For these reasons, commercial specifications in the United States require total acid numbers in oils to be below 0.1, as determined by either of two ASTM test methods disclosed below while European commercial specifications generally require total acid numbers below 0.2.

Mercaptans are objectionable in fuel oils employed in homes or industrial plants primarily because they are strongly and unpleasantly odiferous materials. Furthermore, they are very volatile and unstable compounds and can present a safety problem if present in excessive amounts. However, the prevailing commercial specification for mercaptans of 30 ppm (maximum), or 0.003 weight percent, is based upon odor considerations as this level represents the threshold at which the presence of mercaptans is detectable by odor. Because of the repugnant odor of mercaptans, a level above 30 ppm of mercaptan in the oil would render the mere presence of a fuel oil obnoxious in a home or industrial establishment. In addition, since mercaptans are mild acids, they can also contribute to a corrosion problem of the oil. Furthermore, a mercaptan content above 30 ppm has been found to contribute to gel-type sludge formation in an oil, causing plugging in pipelines in which the oil is standing or flowing.

In accordance with the present invention, an extremely mild hydrogenation treatment has been developed for the reduction of total acid number and/or mercaptan sulfur content in virgin oils which already meet commercial total sulfur content requirements, i.e., a maximum sulfur content below 0.2 weight percent sulfur for home heating fuels. The present invention accomplishes a reduction in total acid number and/or mercaptan sulfur content in oils which already meet commercial total sulfur content requirements without blending such oils with high total sulfur content oils prior to hydrodesulfurization of high total sulfur content oils under severe conditions, as has been the practice in the past. High total sulfur content oils not only require treatment in a high pressure and temperature hydrodesulfurization unit to accomplish hydrodesulfurization, but also require a highly active hydrogenation catalyst. Such conditions will automatically reduce excessive total acid numbers and excessive mercaptan sulfur contents to commercially acceptable values. However, where a straight run middle distillate al
ready meets commercial total sulfur requirements we have now found that total acid number and mercaptan content can be reduced under much milder hydrogenation conditions with a degenerated and deactivated hydrogenation catalyst so that such feeds can be separately treated in another reactor without unnecessarily consuming valuable space in high pressure reactors. There has not previously been a sufficiently mild hydrogenation process to make independent hydrogenation of these oils economic and therefore in hydrogenative treatment they formerly were reduced in total acid number or mercaptan sulfur content by aqueous caustic treatment. However, this method may soon have to be abandoned because the aqueous effluent from caustic units represents an unacceptable stream pollutant under present-day environmental standards.

We have now discovered that the degree of hydrogenation required for the reduction of total acid number or mercaptan sulfur content in virgin middle distillates to acceptable commercial levels where the nature of the crude oil source of these oils is such that these oils already satisfy commercial total sulfur requirements, is so low that it is commercially wasteful to blend these oils with hydrodesulfurization feeds wherein the nature of the crude oil source of the oil is such that a major portion of the total sulfur content of the feed must be also reduced. We have discovered that hydrogenative treatment for reduction of total sulfur requires treatment under hydrodesulfurization conditions which are unnecessarily severe for the low sulfur feeds of this invention. For example, we have found that straight run middle distillates which do not satisfy commercial total acid number and/or mercaptan content requirements but do satisfy commercial total sulfur requirements without hydrotreatment can be separately treated to produce commercially acceptable levels in regard to total acid number and/or mercaptan content in units wherein chemical consumption requirements are only from one to five, or even lower, standard cubic feet of hydrogen per barrel of feed (from 0.018 to 0.09 standard cubic meters per 100 liters of feed) and unit hydrogen consumption including hydrogen losses are less than 10 or 15 standard cubic feet per barrel of feed (less than 0.18 to 0.27 standard cubic meters per 100 liters of feed). The catalytic activity required to accomplish such a slight chemical hydrogen consumption is so correspondingly slight that use of an active or fresh hydrodesulfurization or hydrogenation catalyst is not only wasteful but accomplishes a level of hydrogenation which is not required by the process. To illustrate, a virgin middle distillate stream is ordinarily relatively olefin-free so that it contains only about one percent by volume of olefins, and these olefins are relatively easy to hydrogenate. However, in accordance with the present invention, these olefins are not hydrogenated to a major extent because such olefin hydrogenation is not generally required to accomplish reduction in total acid number or to accomplish reduction in mercaptan content to commercially acceptable levels. However, if the hydrogenation conditions of the present invention were sufficiently severe, saturation of these olefins of itself would account for a chemical consumption of hydrogen of about nine standard cubic feet per barrel (0.162 standard cubic meters per 100 liters), which is higher than that generally required for the reduction for total acid number and mercaptan content in most feeds. In order to diminish unnecessary chemical or unit hydrogen consumption beyond that which is required to reduce neutralization number and/or mercaptan sulfur content in a feed stream of this invention to commercially acceptable levels, the present invention ordinarily employs hydrogen pressures below 100 psig (7 kg/cm²) and also employs as a hydrogenation catalyst a permanently deactivated catalyst as a fixed compact bed in downflow operation, which catalyst has been previously employed in a separate but high pressure (600 psig or more, 4.2 kg/cm² or more) hydrogenation process. The catalyst is only transferred from the severe hydrogenation process after it has experienced many regeneration cycles and its activity loss as compared to its original cycle is so severe that it is no longer a viable catalyst in a high pressure, high hydrogen consumption process except by the use of excessive start-of-run temperatures, or unacceptably short cycle life before further regeneration is required. We have discovered, in accordance with the present invention, that these apparently hopelessly deactivated high pressure hydrogenation catalysts which would otherwise be discarded or decomposed for recovery of valuable metals have a vestige of hydrogenation activity remaining which is sufficient for the process of the present invention. It is emphasized, that the catalysts of the present invention would otherwise be discarded or destroyed as being of insufficient activity to be of further use in other refinery hydrogenation processes. These deactivated catalysts can be subjected to a final combustion regeneration for removal of carbon and a sulfidation within their original reactor and at the temperature of their original reactor, prior to transfer to the mild temperature and pressure reactor of this invention. We have successfully employed in the process of this invention Group VI and Group VIII metal on alumina hydrogenation catalysts, such as NiCoMo on alumina, which have experienced at least four or five regenerations by combustion of carbon until in about the fifth cycle the required start-of-run temperature to accomplish a given product sulfur level in a fuel oil hydrodesulfurization process was elevated by 40⁰ to 60⁰F. (22.2⁰ to 33.3⁰C.) as compared to the initial cycle, thereby rendering the duration of its useful life in the fifth cycle, employing rising temperatures to compensate for desulfurization activity loss, unacceptably short. We have also employed in the process of this invention a deactivated nickel-tungsten-fluorine on silica-alumina hydrocracking catalyst which was sufficiently deactivated so that it was sufficiently inactive for further use as a compact fixed or stationary bed hydrocracking catalyst in downflow operation but still retained sufficient hydrogenation activity to be of use under the mild conditions of this invention wherein the temperatures and pressures were too low to effect significant feed cracking but were sufficient for very mild hydrogenation. Residue hydrosulfurization catalyst permanently deactivated in downflow operation as a compacted bed by feed metals can also be employed in the present invention without prior demetallization. The only pretreatment required for these catalysts is after their removal in their original processes and prior to similar downflow compact bed use in the process of the present invention is a possible combustive regeneration and/or a possible sulfidation step, such as by passage of a high total sulfur-content oil over the catalyst under hydrodesulfurization conditions, after which these catalysts can be
removed from their original reactor to another or secondary reactor, preferably of smaller wall thickness and of different diameter. In their secondary reactor, these catalysts can be employed under low temperature and pressure conditions for a long or indefinite duration, often without further sulfidation or regeneration. We have found the small, residual hydrogenation activity remaining in these catalysts is ample for their employment to accomplish the limited hydrogenation required for the present invention. The following data show that the residual hydrogenation activity present in these aged catalysts is sufficient for reduction of total acid number via neutralization of naphthenic acids by a major extent, such as 75, 80 or 90 percent or more, and by reduction of mercaptan sulfur content via hydrogenation of mercaptan sulfur molecules by a major extent such as by 60, 75, 80 or 90 percent or more, but is insufficient to concomitantly reduce total sulfur by more than a minor amount, i.e., by not more than 10, 20, 30, 40 and less than 50 percent, and is also insufficient to reduce olefin content by more than a minor extent, i.e., not more than 20, 40 and less than 50 percent.

The process conditions for the present invention include temperatures between 300° and 600°F. (149° and 315°C.), generally, and 400° to 550°F. (204° and 288°C.), preferably, hydrogen pressures below 100 or 150 psi (7 and 10.5 kg/cm²), generally, and below 75 psi (5.15 kg/cm²), preferably, liquid hourly space velocities between 3 and 10, generally, and between 4 and 8, preferably and hydrogen circulation rates between 200 and 1,200 SCF/B (3.6 and 21.6 standard cubic meters per 100 liters), generally, and 300 to 1,000 SCF/B (5.4 to 18 standard cubic meters per 100 liters), preferably. Hydrogen pressure requirements for this invention are very low. Generally, only sufficient pressure to move the reactants through the system at the required space velocity will be adequate. A wide variety of Group VI and Group VIII catalytic metals are suitable for the present invention. For example, nickel-cobalt-molybdenum on alumina, cobalt-molybdenum, nickel-tungsten or nickel-molybdenum. The support can be alumina, alumina-silica or silica-magnesia, as long as non-creating conditions are employed.

To illustrate the present invention, in one domestic refinery operation for the preparation of both sulfur and low home heating fuels and also kerosenes boiling broadly in the 350° to 700°F (176° to 371°C.) range or, more narrowly, in the 400° to 650°F (204° to 343°C.) range, the refinery was supplied by five different feed stocks boiling within these ranges originating from different crude sources. These five feed stocks are described in Table 1. Two of the feed stocks, a straight run West Texas kerosene and a West Texas straight run furnace oil did not meet commercial requirements in regard to total sulfur content and therefore required high pressure hydodesulfurization. A furnace oil from a distillation column to which an Orдовician crude was fed contained only 0.11 weight percent total sulfur, meeting commercial specifications, but contained 0.041 weight percent of mercaptans and had a total acid number less than 0.03, thereby failing to meet commercial specifications in regard to mercaptan content (30 ppm maximum) only, while meeting commercial specifications in regard to total acid number (0.1 maximum). A furnace oil from a distillation column to which a South Louisiana crude was supplied contained only 0.10 weight percent total sulfur thereby meeting commercial specifications, contained a mercaptan sulfur content of 0.0004, also meeting commercial specifications, but had a total acid number of 0.46–7, which is above the commercial specification of 0.1. A kerosene derived from a South Louisiana crude met commercial specifications in regard to total sulfur, mercaptan content, but not in regard to total acid number, having a total acid number of 0.12 which exceeds the maximum allowable 0.10 commercial specification. The various feed stocks shown in Table 1 show that it is possible for a straight run middle distillate feed stock to meet commercial specifications in regard to total sulfur content and in regard to total acid number, but not in regard to mercaptan sulfur content. It is also possible for a straight run feed stock to meet commercial specifications in regard to total sulfur content and mercaptan sulfur content, but not in regard to total acid number. It is also possible for a straight run middle distillate to meet commercial specifications in regard to total sulfur content but not in regard to either total acid number or mercaptan sulfur content.

In accordance with the present invention, any straight run feed stock which fails to meet commercial specifications in regard to total sulfur content must be treated in a high pressure vessel capable of accommodating a pressure of 600 to 1,000 psig (42 to 70 kg/cm²) or more and a temperature of 650°F. (360°C.) or more to accomplish hydodesulfurization in the presence of a highly active hydodesulfurization cataly, such as a Group VI and Group VIII metal on a non-cracking support, such as alumina, with or without less than about 1 percent of a non-cracking stabilizing amount of silica, usually in downflow-operation of feed oil and hydrogen. Common catalytic metals include nickel, cobalt, molybdenum, tungsten, etc. in various combinations. However, we have now found that straight run middle distillates which meet commercial total sulfur requirements but fail to meet commercial requirements in regard to total acid number and/or mercaptan sulfur content can be charged to a separate reactor, and at a relatively lower temperature which is always below 650°F. (334°C.), operated at a much lower pressure, such as 100 psig (7 kg/cm²), or less, with the same or a similar catalyst as was used in the high pressure hydodesulfurization reactor as a downflow, compact bed but in a permanently deactivated state in regard to the requirements of the high pressure reactor. In this manner, a smaller total flow is passed through the high pressure reactor, said flow being diminished by the feed charged directly to the low pressure reactor, permitting the diameter of the high pressure reactor to be greatly reduced. Since the thickness of the steel wall which is required in a high pressure and high temperature reactor increases greatly with reactor diameter (by contrast, it is known that a thin-walled copper tube can withstand thousands of pounds of pressure if its diameter is only about one-quarter of an inch or 0.63 cm), the present invention permits the high pressure and temperature reactor to be constructed with a smaller diameter and also with a greatly diminished metal thickness, resulting in considerable economic savings. Since the feed streams bypassing the high pressure reactor are hydrotreated at only 100 psig (7 kg/cm²) or less, and at a lower temperature, i.e., below 500° or 450°F. (260° or 232°C.), than the high pressure reactor, the low pressure reactor will have a
greatly reduced steel thickness, as compared to the high pressure reactor, resulting in a considerable overall savings in the fabrication costs in the metal reactors.

The detailed characteristics of the five middle distillate fuel stocks described above are shown in Table 1, below.

### TABLE 1

<table>
<thead>
<tr>
<th>Inspection</th>
<th>Furnace Oil</th>
<th>Furnace Oil</th>
<th>Kerosene</th>
<th>Kerosene</th>
<th>Furnace Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity, D287</td>
<td>43.9</td>
<td>36.5</td>
<td>43.3</td>
<td>40.0</td>
<td>36.9</td>
</tr>
<tr>
<td>Distillation, °C</td>
<td>321(160°C)</td>
<td>361(183°C)</td>
<td>331(166°C)</td>
<td>348(171°C)</td>
<td>338(170°C)</td>
</tr>
<tr>
<td>End Point</td>
<td>617(325°C)</td>
<td>654(345°C)</td>
<td>490(258°C)</td>
<td>567(297°C)</td>
<td>708(375°C)</td>
</tr>
<tr>
<td>5%</td>
<td>372(189°C)</td>
<td>424(218°C)</td>
<td>359(182°C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10%</td>
<td>385(196°C)</td>
<td>446(230°C)</td>
<td>367(186°C)</td>
<td>393(201°C)</td>
<td>413(212°C)</td>
</tr>
<tr>
<td>20%</td>
<td>407(206°C)</td>
<td>480(249°C)</td>
<td>375(201°C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30%</td>
<td>423(217°C)</td>
<td>496(258°C)</td>
<td>383(195°C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40%</td>
<td>443(228°C)</td>
<td>508(266°C)</td>
<td>390(190°C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50%</td>
<td>463(240°C)</td>
<td>520(271°C)</td>
<td>399(204°C)</td>
<td>452(233°C)</td>
<td>499(259°C)</td>
</tr>
<tr>
<td>60%</td>
<td>487(253°C)</td>
<td>532(278°C)</td>
<td>408(209°C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>70%</td>
<td>513(267°C)</td>
<td>548(287°C)</td>
<td>419(215°C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80%</td>
<td>541(283°C)</td>
<td>566(297°C)</td>
<td>432(223°C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90%</td>
<td>573(300°C)</td>
<td>596(313°C)</td>
<td>452(235°C)</td>
<td>520(271°C)</td>
<td>630(322°C)</td>
</tr>
<tr>
<td>95%</td>
<td>595(313°C)</td>
<td>622(328°C)</td>
<td>466(241°C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sulfur, weight percent</td>
<td>.11</td>
<td>.10</td>
<td>-</td>
<td>.69</td>
<td>.92</td>
</tr>
<tr>
<td>Sulfur, ppm</td>
<td>-</td>
<td>-</td>
<td>267</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mercapta Sulfur, D1233</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>weight percent</td>
<td>.04</td>
<td>.0004</td>
<td>.0006</td>
<td>.127</td>
<td>.11</td>
</tr>
<tr>
<td>Total acid number, D974</td>
<td>&lt;.03</td>
<td>.47</td>
<td>12</td>
<td>.06</td>
<td>-</td>
</tr>
<tr>
<td>Total acid number, D664</td>
<td>-</td>
<td>.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bromine number, D1159</td>
<td>-</td>
<td>-</td>
<td>6.7</td>
<td>7.4</td>
<td>-</td>
</tr>
</tbody>
</table>

No additional catalyst cost is required for operation of the low pressure reactor, which is the reactor of the present invention, since it operates with catalyst that has been deactivated by repeated regenerations in the high pressure reactor until it is no longer of commercial utility in the high pressure reactor. The deactivated high pressure catalyst is sulfided if required in the high pressure reactor proximate to withdraw from there at a temperature of about 600°F to 650°F. (315° to 330°C) by passage of high sulfur-content oil through. If required, it can also be regenerated by combustion in the high pressure reactor. Then the catalyst can be removed from the high pressure reactor by any suitable means, such as through a plug in the bottom thereof. The catalyst for reuse in the low pressure reactor can comprise the catalyst from the high pressure reactor in its entirety, or, since feed oil is passed downward through the high pressure reactor, the reused catalyst can comprise only the bottom bed of a multiplicity of beds, or can comprise a portion of a single bed contained in the high pressure reactor, omitting the uppermost region of the bed, thereby utilizing in the low pressure reactor only the cleanest, most metals-free portion of the catalyst from the high pressure reactor. It is possible to utilize the entire bed from the high pres-

Table 2, below, shows the test conditions employed and the results obtained when the first three feed stocks listed in Table 1 (which already met commercial total sulfur requirements and therefore did not require high pressure hydrosulfurization) were treated under the low pressure hydrogen test conditions of this invention with aged (deactivated) catalysts for the reduction of mercaptan sulfur content and/or total neutralization number only. In all tests, the feed oil and hydrogen were passed downwardly over a fixed, stationary, compact catalyst bed.

### TABLE 2

<table>
<thead>
<tr>
<th>Feed From Table 1</th>
<th>Ordovician Furnace Oil</th>
<th>South Louisiana Furnace Oil</th>
<th>South Louisiana Kerosene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Conditions:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td>Aged</td>
<td>Aged</td>
<td>Aged</td>
</tr>
<tr>
<td>Reactor Temperature, °C</td>
<td>500(260°C)</td>
<td>475(246°C)</td>
<td>450(232°C)</td>
</tr>
<tr>
<td>Reactor Pressure, psi</td>
<td>100(7 kgs/cm²)</td>
<td>100(7 kgs/cm²)</td>
<td>100(7 kgs/cm²)</td>
</tr>
<tr>
<td>Space Velocity, Vol/Hr/Vol</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Gas Circulation Rate:</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>(18 m³/100 liters)</td>
<td>(18 m³/100 liters)</td>
<td>(18 m³/100 liters)</td>
<td></td>
</tr>
<tr>
<td>Gas Hydrogen Content:</td>
<td>85</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Volume percent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid Product Yield:</td>
<td>85</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Volume percent FF</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Hydrogen Sulfide Yield:</td>
<td>0.06</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Weight percent FF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh Feed</td>
<td>Hydrotreated Product</td>
<td>Fresh Feed</td>
<td>Hydrotreated Product</td>
</tr>
</tbody>
</table>
Table 2 shows that the present process improves not only mercaptan sulfur content and total acid number but also improves color properties of the feed oil. It also shows there is substantially 100 percent yield of furnace oil or kerosene in the present process.

Table 3, presented below, presents additional test data and product specifications when treating the Or dovician furnace oil under still other single pass conditions than those shown in Table 2.

### Table 3

<table>
<thead>
<tr>
<th>Feed From Table 1</th>
<th>Ordivician Furnace Oil</th>
<th>South Louisiana Furnace Oil</th>
<th>South Louisiana Kerosene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity, D287: API</td>
<td>43.9</td>
<td>43.8</td>
<td>36.5</td>
</tr>
<tr>
<td>Distillation, D66: °F</td>
<td>321(161°C)</td>
<td>338(170°C)</td>
<td>361(182°C)</td>
</tr>
<tr>
<td>Over Point</td>
<td>617(323°C)</td>
<td>629(332°C)</td>
<td>654(345°C)</td>
</tr>
<tr>
<td>10%</td>
<td>385(196°C)</td>
<td>388(198°C)</td>
<td>464(230°C)</td>
</tr>
<tr>
<td>30%</td>
<td>423(217°C)</td>
<td>431(222°C)</td>
<td>496(258°C)</td>
</tr>
<tr>
<td>50%</td>
<td>446(239°C)</td>
<td>474(245°C)</td>
<td>520(271°C)</td>
</tr>
<tr>
<td>70%</td>
<td>513(267°C)</td>
<td>523(275°C)</td>
<td>548(287°C)</td>
</tr>
<tr>
<td>90%</td>
<td>573(301°C)</td>
<td>583(306°C)</td>
<td>596(313°C)</td>
</tr>
<tr>
<td>Mercaptan Sulfur, D1323, weight percent</td>
<td>0.041</td>
<td>0.0009</td>
<td>0.0004</td>
</tr>
<tr>
<td>Total Acid Number, D974</td>
<td>&lt;0.03</td>
<td>—</td>
<td>0.47</td>
</tr>
<tr>
<td>Sulfur, ppm</td>
<td>—</td>
<td>262.0</td>
<td>—</td>
</tr>
<tr>
<td>Sulfur, weight percent</td>
<td>0.11</td>
<td>0.05</td>
<td>—</td>
</tr>
<tr>
<td>Color, Saybolt, D156</td>
<td>+14</td>
<td>+17</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 3 shows the relationship in the process of the present invention between non-mercaptan or total sulfur content reduction and mercaptan desulfurization number reduction in tests conducted at 100 psig (7 kg/cm²), 400° to 650°F. (204° to 343°C), 4.8 LHSV, 300 - 1,000 SCF (85% H₂)/B (5.4-18 SCM/100L). The solid circles of FIG. 1 represent the Ordivician furnace oil feed of Table 1 while the crosses indicate the West Texas kerosene feed of Table 1. As shown in
FIG. 1, the process of this invention removed about 90 weight percent of the mercaptan sulfur before removing only about 15 percent of the total sulfur content of the feed, showing the high selectivity of the present process for removal of mercaptan sulfur while not removing total sulfur. FIG. 1 shows a 50 percent reduction in mercaptan sulfur content occurred with only about 1 to 2 percent reduction in total sulfur content.

FIG. 2 shows the relationship between non-mercaptop or total desulfurization and percent reduction in total acid number with tests conducted under the conditions of the present invention which include 100 psig (7 kg/cm²), 400⁰ to 650⁰F. (204⁰ to 343⁰C.), 4–8 LHSV and 300–1,000 SCF (85.5% H₂)/B (5.4–18 SCM/100L). In FIG. 2, the crosses indicate the South Louisiana kerosene feed of Table 1 and the solid circles indicate the South Louisiana furnace oil feed of Table 1. FIG. 2 shows that the process of the present invention is capable of reducing the total acid number of a feed oil by at least 80 percent while reducing the total sulfur content of the oil only 20 percent, again showing the high selectivity of the present process for treatment of low total sulfur-containing oils. FIG. 2 shows a 50 percent reduction in total acid number occurred with less than about a five percent reduction in total sulfur content.

FIGS. 1 and 2 both show that the reduction in mercaptan sulfur content and the reduction in total acid number both occur much more readily than the undesired total desulfurization reaction. FIGS. 1 and 2 show that 90–95 percent mercaptan desulfurization and 80 percent total acid number reduction occur with only 20 percent total desulfurization.

FIG. 3 illustrates the results of a similar test with the same aged catalyst at 100–150 psig (7–10.5 kg/cm²). The solid circles represent a heavy FCC naphtha feed (not illustrated in Table 1), the hollow circles represent the West Texas kerosene feed of Table 1, and the triangles represent the West Texas furnace oil feed of Table 1. FIG. 3 shows that the saturation of olefins occurs at even a slower rate than non-mercaptop or total desulfurization, i.e., at 20 percent total desulfurization only about 6 percent olefin saturation occurred. Therefore, the conditions of the present invention are too mild to accomplish significant olefin saturation. This is an important feature of the present invention because, assuming a typical middle distillate feed contained 1 percent olefin by volume, the saturation of these olefins alone would account for a chemical hydrogen consumption of about 9 SCF/B (0.162 SCM/100L).

FIGS. 4, 5 and 6 show results obtained with a fresh hydrogenation catalyst having a similar composition as that employed in the tests of the other Figures, except that the catalyst represented by the lowest curve of FIG. 4 was previously aged for two cycles in a prior high pressure hydrogenation process. These figures show that the present invention can be practiced with a fresh as well as an aged catalyst, although the fresh catalyst will require milder conditions to maintain the low hydrogen consumption levels of this invention. In FIGS. 4, 5A and 5B the feed stock is the Ordovician furnace oil of Table 1. The tests of FIG. 4 were performed with a circulation of 1,000 SCF/B (18 SCM/100L) of 85 percent hydrogen at the temperatures, pressures and space velocity conditions indicated. FIG. 4 shows that in accordance with the present invention the feed mercaptan sulfur content can be reduced from a value of 410 in the original feed stock to values as low as 8, 10 or 20 ppm at 450°F. (232°C.), and can be reduced to a value approaching 0 ppm at a temperature of 500°F. (260°C.). FIG. 4 shows very little advantage in increasing the pressure from 100 to 200 psi (7 to 14 kg/cm²) for removal of mercaptan sulfur. FIG. 4 also shows that more than 90 percent mercaptan removal occurred in the process for the feed oil to meet the commercial specification of 30 ppm mercaptan content.

FIGS. 5A and 5B, represent tests made with the Ordovician furnace oil feed to Table 1 and show that hydrogen circulation rate does not have a great effect upon the achievement of 30 ppm of mercaptan sulfur in the oil at the conditions tested.

The tests of FIG. 6 were made with the South Louisiana furnace oil to Table 1 at 100 psig (7 kg/cm²) with 1,000 SCF/B (18 SCM/100L) of 85 percent hydrogen. These tests show that feed total acid number can be reduced in a feed which had a value of 0.47, to a value of 0.1 at temperatures below 450⁰ to 500⁰F. (232⁰ to 260⁰C.) depending upon space velocity. FIG. 6 shows that nearly 80 percent reduction in acid content occurred in the process for the feed oil to meet the commercial specification of 0.1 total acid number.

FIGS. 4, 5A, 5B and 6 illustrate that a wide range of low severity temperature, pressure and space velocity conditions can be employed with a hydrosulfurization catalyst to accomplish the required commercial low mercaptan sulfur content and low total acid number values in accordance with this invention.

As stated above, commercial specifications for No. 2 furnace oil require a maximum total sulfur content of 0.2 weight percent sulfur for home heating fuel, a maximum mercaptan content of 30 ppm (0.003 weight percent) and a total acid number of less than 0.1. Total acid number is defined as milligrams of potassium hydroxide (KOH) that is required to neutralize all acidic constituents present in 1 gram of oil sample (mg KOH/gm sample), according to ASTM test D664 or D974, 1968 Book of ASTM Standards, Volume 17, page 235. About the same results are obtained in total acid number when ASTM test method D974, which employs colorimetric titration, is employed, as in the case of method D664, which employs potentiometric titration. Mercaptan sulfur content is defined as grams of mercaptan sulfur per 10⁶ grams of oil.

It is seen that of the middle distillates listed in Table 1, only the West Texas middle distillates contained more than commercial specifications in regard to total sulfur content. Therefore, it is necessary to hydrosulfurize these oils at a pressure above 600 psig (42 kg/cm²), and preferably in the 1,000 to 2,000 psig (70 to 140 kg/cm²) range disclosed above to reduce their sulfur content to 0.2 weight percent sulfur. However, the Ordovician middle distillate and the South Louisiana middle distillates both meet commercial total sulfur content requirements and therefore do not require severe hydrosulfurization to accomplish reduction of total sulfur content. However, under the practice of the prior art, the Ordovician and South Louisiana middle distillates would have been blended with the West Texas middle distillates to obtain a total refinery middle distillate blend for feeding to the high pressure hydrosulfurization unit because under the severe hydrogenation conditions required for the reduction of total sulfur content of the West Texas middle distil-
lates, the 410 ppm mercaptan content of the Ordovician middle distillate would easily be reduced to the commercially acceptable 30 ppm mercaptan content and the 0.46–7 total acid number of the South Louisiana middle distillates would easily be reduced to the commercially acceptable total acid number of less than 0.1. However, in accordance with the present invention, virgin middle distillates, prior to hydrogenation or other treatment, in which state they ordinarily contain less than one percent olefin, are not sent to the high pressure hydrosulfurizer but rather are hydrodetermed in a separate reactor under much more economic and mild conditions at a great savings of space in the high pressure reactor. This practice is based upon our discovery that for straight run middle distillates the severity of the operation required for the reduction of total acid number and the reduction of mercaptan sulfur content by hydrotreatment is much milder than is required for the reduction of total sulfur content.

The following calculations are presented to illustrate that relatively minuscule quantities of chemical hydrogen consumption are required to accomplish the required reductions in total acid number and mercaptan sulfur content in accordance with this invention.

To reduce the total acid number via hydrogenation, the most prevalent reaction involved is the reaction of an organic naphthenic acid with hydrogen to produce a saturated hydrocarbon plus water, according to the following equation:

\[ R - \text{C} = \text{O} + 3\text{H}_2 \rightarrow R - \text{CH}_3 + 2\text{H}_2\text{O} \]

From this equation it is seen that three moles of hydrogen are required to saturate one mole of organic acid. The hydrogenation method of neutralization is the method employed in accordance with the present invention.

The ASTM neutralization test method reacts the organic acid with KOH to produce a salt plus water according to the equation:

\[ R - \text{C} = \text{O} + \text{KOH} \rightarrow \left( R - \text{C} = \text{O}^{-}\right) + \text{K}^+ + \text{H}_2\text{O} \]

It is seen from this equation that one mole of KOH is required to neutralize one mole of organic acid.

If the neutralization or total acid number of a feed oil is known, the amount of hydrogen required to be consumed when reducing the total acid number to the value required by commercial specifications can be calculated as follows:

Total acid number = \((\text{mg KOH}/\text{gram sample}) \times \rho_{\text{oil}} \times \text{density of sample, gm/cc} \times \text{Molecular weight of KOH = 56, 108 mg/mole} \)

\[ \Delta \text{total acid number} = \text{reduction in total acid number} \]

\[ \text{(total acid number of untreated oil minus the acid number of the treated product)} \]

\[ \text{H}_2 \text{ consumption (SCF/Bbl)} = \Delta \text{ total acid no.} \times \rho_{\text{oil}} \times (1/56,108) \times (1 \text{ mole KOH/453.6 gm moles}) \times (379 \text{ SCF/no. mole}) \]

\[ = ((\Delta \text{ total acid no.}) \times (3785) \times (42.0) \times (379)/(56,108) \times (453.6) \text{ SCF H}/\text{Bbl}) \]

\[ = (\Delta \text{ total acid no.}) \times (7.10) \text{ SCF H}/\text{Bbl} \]

To convert SCF H/Bbl oil to SCM/100L multiply by 0.018.

In an actual example based on the South Louisiana middle distillate of Table 1 which has a total acid number of 0.46 wherein the specific gravity of the oil was 36.5°API (0.8423 g/cc), to reduce the total acid number (Δ total acid number) from 0.46 to 0.10 (Δ = 0.36) the hydrogen consumption is therefore the (Δ total acid number) times the density of the oil times 7.10; or Hydrogen consumption = 0.36 \times 0.8423 \times 7.10 = 2.2 standard cubic feet of hydrogen per barrel (0.04 SCM/100L).

It is seen from the above sample calculation that the hydrogen requirement to reduce the total acid number of the South Louisiana middle distillate to meet commercial standards is extremely small, as long as the middle distillate already meets commercial standards in regard to total sulfur content. Therefore, in accordance with this invention not more than about 5 to 10 standard cubic feet of hydrogen per barrel (0.09 to 0.18 SCM/100L) of middle distillate are required in terms of chemical hydrogen consumption to reduce total acid number of an oil sufficiently to meet commercial requirements of the oil. In terms of total unit hydrogen requirement, including solubility losses, the requirement in hydrogen need not exceed 15, 20, 25 or 30 standard cubic feet per barrel (0.27, 0.36, 0.45 or 0.54 SCM/100L).

It can be commercially that hydrogen requirements for reducing mercaptan sulfur content to commercially acceptable levels by hydrogen treatment in accordance with the present invention can be even smaller than that shown above for the reduction of total acid number. The reaction involved for the reduction of mercaptan sulfur via hydrogenation proceeds as follows:

\[ R - \text{CH}_3 + 2\text{H}_2 \rightarrow R - \text{CH}_3 + \text{H}_2\text{S} \]

From the above equation, it is seen that two moles of hydrogen are required for each mole of mercaptan sulfur which is removed.

The analysis of mercaptans is usually presented in units of parts per million, as follows:

\[ \text{Mercaptan sulfur content} = (\text{gms mercaptan sulfur/100 gms oil}) \]

\[ \Delta \text{ Mercaptan sulfur content} = \text{mercaptan sulfur in charge (ppm) minus mercaptan sulfur in product (ppm)} \]

\[ \text{Molecular weight of oil} = \text{MW}_{\text{oil}} \text{ (grams of oil/gm-mole oil)} \]

Assuming that the molecular weight of the mercaptan compound in the oil is approximately the same as the molecular weight of the oil,

\[ \text{Hydrogen consumption in SCF/Bbl for mercaptan removal} = \Delta \text{ Mercaptan S content (gms Mercaptan S/106 gms oil)} \times \rho_{\text{oil}} \times (3785 \text{ cc/gal}) \times (42.0 \text{ gal/Bbl}) \times (1/\text{MW mercaptan/gms}) \times (\text{MW} \times 2 \text{ gm moles H/gm mole mercaptan}) \times (1 \text{ no. mole/453.6 gm moles}) \times (379 \text{ SCF/1 no. mole gas}) \]
The Orlovpanic middle distillate shown in Table 1 contained 410 ppm of mercaptan. Its API was 43.9\(^\circ\) (8.067 gm/cc). Its mean average boiling point was 451\(^\circ\)F. (233\(^\circ\)C). Its molecular weight, from API and mean average boiling point, is 192. Therefore, to reduce the mercaptan sulfur in the charge from 0.041 weight percent, or 410 ppm, to a product containing 30 ppm, the hydrogen consumption = [(410 - 30) (8.067) (0.266)/192] = 0.4 standard cubic feet per barrel (0.0072 SCM/100L).

It is seen from the above sample calculation that the hydrogen requirement to reduce the mercaptan content of the Orlovpanic middle distillate to meet commercial standards is extremely small, as long as the middle distillate already meets commercial standards in regard to total sulfur content. Therefore, in accordance with this invention not more than about 5 to 10 standard cubic feet of hydrogen per barrel of middle distillate (0.09 or 0.18 SCM/100L) are required in terms of chemical hydrogen consumption to reduce mercaptan content of an oil sufficiently to meet commercial requirements of the oil. In terms of total unit hydrogen requirement, including solubility losses and losses in the hydrogen off-gas, the requirement in hydrogen need not exceed 15, 20 or 25 standard cubic feet per barrel (0.27, 0.36 or 0.45 SCM/100L). According to the Oil and Gas Journal, February 17, 1969, Volume 67, No. 7, page 78, hydrogen solubility losses are about 0.4 SCF/B (0.0072 SCM/100L) times the pressure in atmospheres. Therefore, at 100 psi (7 kg/cm\(^2\)) unit pressure, hydrogen solubility losses are 0.4 times 100/15 = 3 SCF/B (0.054 SCM/100L). Table 3 shows total unit hydrogen requirements of only 14 standard cubic feet per barrel (0.0252 SCM/100L) when treating the Orlovpanic middle distillate of Table 1.

The above two calculations show the actual mercaptan sulfur removal or acid number reduction is accomplished with hydrogen chemical consumptions only slightly above zero to less than 3 standard cubic feet per barrel (0.054 SCM/100L).

It is again seen that for a middle distillate which meets commercial requirements in regard to total sulfur content, the hydrogen consumption requirement for the reduction of mercaptan sulfur to commercially acceptable levels is extremely small and can be below 1 and generally will not exceed 5 or 10 standard cubic feet per barrel (0.09 or 0.18 SCM/100L) in terms of chemical hydrogen consumption, or will not exceed 15, 20 or 25 standard cubic feet per barrel (0.027, 0.36 or 0.450 SCM/100L) in terms of total unit hydrogen consumption, including losses. In fact, when a feed meets commercial total sulfur requirements but does not meet commercial total acid number requirements or commercial mercaptan content requirements, the total chemical consumption to meet both of these requirements should not exceed 5 to 10 standard cubic feet per barrel (0.09 or 0.18 SCM/100L), 15 to 25 standard cubic feet per barrel (0.27 to 0.45 SCM/100L) when solution losses are considered.

We claim:
1. A relatively low pressure process for hydrotreating a straight run No. 2 home heating fuel oil feed having a total sulfur content of less than 0.2 weight percent, comprising passing said oil over a hydrotreating catalyst, said straight run feed oil having a total acid number greater than 0.1 as determined by ASTM test D664 or D974, the pressure in said process being no greater than about 150 psi, the temperature in said process being from 400\(^\circ\)F to below 500\(^\circ\)F., hydrogen consumption including solution losses in said process being no greater than about 25 standard cubic feet of hydrogen per barrel of feed oil, and recovering an effluent oil having a total acid number no greater than 0.1.
2. The process of claim 1 wherein said hydrotreating catalyst previously has been used in a relatively high pressure hydrotreating process.
3. The process of claim 1 wherein said hydrotreating catalyst previously has been used in a relatively high pressure hydrotreating process until it has been substantially permanently deactivated for purposes of said high pressure process.
4. The process of claim 1 wherein the catalyst comprises supported Group VI and Group VIII metals and the pressure is no greater than 100 psi.
5. The process of claim 1 wherein the temperature is below 450\(^\circ\)F.
6. The process of claim 1 wherein the LHSV is between 4 and 8.
7. The process of claim 1 wherein the total acid number of the feed oil is reduced at least about 80 percent while the total sulfur content of the feed oil is reduced not more than 40 weight percent.
8. The process of claim 1 wherein the total acid number of the feed oil is reduced at least about 80 percent while not more than about 20 weight percent of the total sulfur content of the feed oil is removed.
9. The process of claim 2 wherein the prior relatively high pressure hydrotreating process is a hydrodesulfurization process operated at a pressure above 600 psi.
10. The process of claim 1 wherein chemical hydrogen consumption excluding solution losses is less than 10 standard cubic feet per barrel of feed oil.
11. The process of claim 1 wherein hydrogen consumption including solution losses is less than 20 standard cubic feet per barrel of feed oil.
12. The process of claim 1 wherein the hydrogen circulation rate is between 200 and 1,200 standard cubic feet per barrel of feed oil.
13. The process of claim 1 wherein the total acid number of said feed oil is above 0.47 or more.
14. The process of claim 1 wherein there is substantially 100 percent yield of said feed oil.
15. A relatively low pressure process for hydrotreating a straight run No. 2 home heating fuel oil feed having a total sulfur content of less than 0.2 weight percent, comprising passing said oil over a hydrotreating catalyst which has been used in a prior relatively high pressure hydrotreating process until it has been substantially permanently deactivated for purposes of said high pressure process, said straight run feed oil having a total acid number greater than 0.2 as determined by ASTM test D664 or D974, the pressure in said process being no greater than about 150 psi, the temperature in said process being from 400\(^\circ\)F to below 500\(^\circ\)F., unit hydrogen consumption including solution losses in said process being no greater than about 30 standard cubic feet of hydrogen per barrel of feed oil, and recovering an effluent oil having a total acid number no greater than 0.2.

* * * * *
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,876,532
DATED : April 8, 1975
INVENTOR(S) : Robert A. Plundo, Thomas C. Readal & James R. Strom

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 13, line 65, "H_a" should read --H_2--

Col. 14, line 63, "= \rho_{oil}" should read -- x \rho_{oil} --

Col. 14, line 65, " (MW x " should read --(MW_{oil}) x ( --

Signed and sealed this 24th day of June 1975.

(Seal)
Attest:
RUTH C. HAGG
Attestign Officer

C. MARSHALL BAHN
Commissioner of Patents
and Trademarks