This invention relates generally to a desulfurization process of petroleum by using pyrophoric reduced iron powders and more particularly it relates to a desulfurization process of crude oil or heavy oil.

Crude oil usually contains various sulfur compounds and, therefore, various petroleum products fractionally produced from the crude oil always contain these sulfur compounds. Such sulfur compounds usually give undesirable influences on the qualities and the properties of the petroleum products except in specific cases.

Therefore, desulfurization processes have been studied in the petroleum refining industry in relation to various petroleum products, such as, gasoline and kerosene, and almost complete desulfurization has been performed by applying various washing methods, catalytic methods, hydro-desulfurization methods etc. to petroleum products having comparatively high economic values such as gasoline or kerosene, and sulfuric acid treatments, solvent-refining methods etc. to lubricating oil.

However, as the costs of oils, such as, crude oil, heavy oil, and light must be kept comparatively low, it is almost impossible under present conditions to adopt economically the above-mentioned processes.

The investigation of conventional desulfurization processes for heavy oil has revealed that the most feasible method is one wherein kerosene and light oil are desulfurized and mixed in heavy oil, but from the heavy oil standard there is a restriction in the mixing amount and hence usually at most about 10% sulfur content in heavy oil can be removed by mixing about 10% kerosene and light oil.

There has also been proposed various other processes, such as, an alkaline-washing method, a propane-deasphalt ing method, a method of utilizing bacteria, a desulfurizing method in which the bonding strength between a carbon atom and a sulfur atom is weakened by the irradiation of radioactive rays, etc., but since these processes are rather high in cost, the possibility that they will be practiced in the future is very poor. Moreover, the supply source of petroleum in the world is now in the Middle East and crude oils from there contain generally a large amount of sulfur and among them the higher the specific gravity is and the lower the cost is, the larger the sulfur content is.

The present invention's objective is to eliminate these drawbacks of the conventional processes. That is, an object of this invention is to provide a very economical desulfurization process for crude oil or heavy oil, which is very suitable for mass production.

Another object of this invention is to provide a desulfurization process for crude oil or heavy oil wherein inexpensive desulfurizing agents can be used.

A further object of this invention is to provide a desulfurization process for petroleum oil or heavy oil wherein the desulfurization can be carried out by an extremely simple process.

A still further object of this invention is to provide a desulfurization process for petroleum oil or heavy oil wherein the spent desulfurizing agents can be used for other useful purposes.

Additional objects of this invention will be understood completely by referring to the following description and claims.

The present invention is a process for removing a part of the sulfur contained in crude oil or heavy oil by contacting sufficiently the crude oil or the heavy oil in the liquid phase or, as the case may be, in the vapor phase, with pyrophoric reduced iron powders. The process is a quite novel one completely different from any conventional desulfurization process for crude oil and heavy oil.

The invention will be explained more in detail hereinafter.

In the first place, pyrophoric reduced iron powders are used in this invention as the desulfurizing agent.

In general, the importance of the pyrophoric property of reduced iron powder should be particularly emphasized because the reduced iron powder having the pyrophoric property is caused to react vigorously with oxygen in air, which makes the reaction with sulfur in crude oil or heavy oil more active, and it is considered that the reaction has an extremely intimate relation with the desulfurization effect.

In general, in the case of producing spongy reduced iron by the gas reduction of an iron ore, the obtained reduced iron has, more or less, the pyrophoric property. However, since the pyrophoric property is usually harmful for general uses of the reduced iron powders, the reduced iron powders must be generally subjected to an ignition-preventing treatment.

The method of the present invention is characterized by just contrarily utilizing this harmful pyrophoric property of the reduced iron powders to perform the most difficult desulfurization of crude oil or heavy oil.

In order to carry out effectively the process of this invention, reduced iron powders having high pyrophoric property must be first produced.

The “pyrophoric property” denotes here a property that when a reduced iron powder is exposed to air, the iron powder ignites and burns.

The main factors for increasing the pyrophoric property are as follows:

1. Using as the reducing gas a gas mainly consisting of hydrogen rather than a gas mainly consisting of carbon monoxide.

2. Reducing at low temperatures.

3. Increasing the reduction ratio.

4. Using a porous iron ore having a small apparent specific gravity.

5. Using an iron ore containing a large quantity of alumina.

Among them, factors 1, 2 and 3 are most important, and an iron ore of factor 4 and/or factor 5 is treated in accordance with factors 1, 2 and 3.

Hence, in this invention the reduced iron powders may be prepared by the following process.

A porous iron ore containing a large quantity of alumina, for instance, laterite or an iron ore containing a large quantity of alumina, such as Durango powder ore, is gas-reduced at temperatures of 500-800°C. in a reducing gas atmosphere, such as, a hydrogen fraction.
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3 gas obtained by a low temperature separation of various by-produced gases containing about 50-80% hydrogen produced in petroleum refining, petroleum-chemistry plants or ironworks, for instance, a coke oven gas, or in a reducing gas atmosphere such as a coke oven gas dry-desulfurized to afford reduced iron powders having the reduction ratio of 50-80%, which are to be stored in a nitrogen atmosphere.

If the reducing temperature is lower than 500° C, the reduction period is too long, which makes the reduction uneconomical, and if the temperature is higher than 500° C, sintering occurs. Further, if the reduction ratio is below 50%, the pyrophoric property is low and if above 80%, the treatment is uneconomical in industry. In addition, when the raw material is not a powdered ore, the raw material is ground into about 30-300 meshes prior to the reduction treatment.

Hitherto, as solid inorganic materials used for the desulfurization of crude oil and heavy oil, alumina and the like have been known, but the use of the reducing iron powders as in this invention was not known. Moreover, even in the conventional case where alumina, etc., is used, they are used as a catalyst for hydro-desulfurization and the desulfurizing agent in this case is hydrogen.

Therefore, the process of this invention wherein the pyrophoric reduced iron powders are used directly as a desulfurizing agent is completely different from the above-mentioned conventional process.

When crude oil or heavy oil contains generally about 2-4 wt. percent sulfur, 10-15% the above-mentioned pyrophoric reduced iron powders based on 1 kg. of such a crude oil or heavy oil are added to the crude oil or heavy oil in an air-free condition, followed by agitation sufficiently for 30 min.-1 hr. Then, the mixture is allowed to stand for about 30 minutes to precipitate the iron powders combined with sulfur and the iron powders combined with sulfur are separated by a conventional filtering method.

By the above treatment, the content of sulfur in the crude oil or heavy oil can be reduced by about 30-50 wt. percent.

As the desulfurization ratio in the case of desulfurizing crude oil or heavy oil may be about 30-80% in general and the desulfurization ratio obtained by the treatment of this invention is above 50%, the invention is sufficiently effective for industry.

In the above-mentioned treatment, it is necessary to add the thus prepared pyrophoric reduced iron powders to crude oil or heavy oil in an inert atmosphere.

Further, as another embodiment of this invention, crude oil or heavy oil may be contacted with the reduced iron powders in the vapor phase by heating the oil. For example, a pipe packed with the reduced iron powders and glass fibers is installed between a distillation still and a cooler in such a manner that the oil may pass through the pipe in the vapor phase.

The process of this invention can be carried out by combining the above-mentioned liquid-phase and gas-phase treatments, whereby the desulfurization ratio can be further increased.

Further, in contrast to the carbon dioxide used in a conventional alkali-washing method or hydrogen in a conventional hydro-desulfurization method, which are lost during the treatment, the pyrophoric reduced iron powders are combined with sulfur in crude oil or heavy oil in some form, when they are used for desulfurization according to the method of the present invention, and the iron powders thus combined with sulfur are separated from the crude oil or heavy oil and effectively utilized as a material for making sulfuric acid or iron source, by supplying them to a roasting furnace for the production of sulfuric acid or to a sintering furnace.

To sum up, the merits of the process of this invention as compared to conventional processes are as follows:

The first point is that the treatment is simple. That is, since the desulfurization of this invention can be carried out by simply contacting crude oil or heavy oil in the liquid phase or, in the alternative, in the vapor phase with the pyrophoric reduced iron powders, such troublesome operation is unnecessary as a conventional hydro-desulfurization method wherein oil is caused to react with hydrogen at a high pressure by using a catalyst.

The second point is that the process of this invention is suitable for a large-scale treating system. As mentioned above, the desulfurization ratio may be 30-80% in the case of desulfurizing crude oil or heavy oil, but the most important point is to treat the oil in large scale and with a reduced cost. As compared with a specific method, such as, a bacteria method or a radioactive method, the treating rate of this invention is comparatively fast and scaling-up is possible in the process of this invention. Therefore, the invention is a process suitable for a large-scale treating system.

The third point is that the cost of the desulfurizing agent in this invention is comparatively low. In general, the cost of reduced iron powders is comparatively high because they are usually produced by reducing with a high reduction ratio a high-quality ore by using very pure hydrogen and also they require the separation of gangue minerals by a magnetic separation and the like. However, as the pyrophoric property is important in the reduced iron powders of this invention, a cheap iron ore such as laterite can be used as the iron ore and the iron ore may be reduced at a low-temperature reduction of about 500-700° C, with a reduction ratio of about 50-80% by using various hydrogen-rich gases produced in petroleum refining, petroleum chemistry plants or ironworks. Therefore, as the cost of the reducing gas itself is low and the reduction can be carried out in a one-pass system without need of a gas-circulating system, which results in reducing the cost of the reducing work, as well as the separation of gangue minerals from the reduced iron is unnecessary, the pyrophoric reduced iron powders for the desulfurization can be produced with an extremely low cost, e.g. at a cost below 1/5% of that of iron powders for powder metallurgy.

The fourth point is that the reduced iron powders used in the desulfurization process of this invention are useful after use in the instant process.

The preferred examples of this invention are as follows.

Example 1

Powdered iron ores shown in the following table were gas-reduced in the reducing gas atmospheres shown in the following table to obtain reduced iron powders, which were stored in a nitrogen atmosphere.

<table>
<thead>
<tr>
<th>Feed ore</th>
<th>Total Fe</th>
<th>As₂O₃</th>
<th>SiO₂</th>
<th>Ni</th>
<th>Cr</th>
<th>TiO₂</th>
<th>C.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manisen-Laterite (A)</td>
<td>45.30</td>
<td>8.11</td>
<td>2.40</td>
<td>6.67</td>
<td>2.68</td>
<td>12.79</td>
<td></td>
</tr>
<tr>
<td>Dungun powdery ore (B)</td>
<td>58.01</td>
<td>7.28</td>
<td>6.08</td>
<td>6.66</td>
<td>4.40</td>
<td>13.35</td>
<td></td>
</tr>
<tr>
<td>Subhaliase sand iron (C)</td>
<td>68.84</td>
<td>6.29</td>
<td>5.69</td>
<td>6.66</td>
<td>5.63</td>
<td>18.34</td>
<td></td>
</tr>
</tbody>
</table>
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Reducing gas

| Hydrogen fraction by low-temperature separation of coke oven gas (a) | 
|---|---|---|---|---|---|---|
| N₂ | CO | CO₂ | CH₄ | C₂H₄ | C₂H₆ |
| 62 | 8 | 0 | 0 | 0 | 0 |

Coke oven gas desulfurized by a dry method (b) | 42 | 7 | 20 | 4 | 1 |

Recovering converter gas (c) | 1 | 5 | 12 | 0 | 0 |

Reduction condition | Ore | Reducing gas | Reducing temp., °C | Reducing ratio, percent | Pyrophoric property
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced iron powder (α)</td>
<td>A</td>
<td>s</td>
<td>850-900</td>
<td>ca. 56</td>
</tr>
<tr>
<td>Reduced iron powder (β)</td>
<td>B</td>
<td>b</td>
<td>700-800</td>
<td>ca. 70</td>
</tr>
<tr>
<td>Reduced iron powder (γ)</td>
<td>C</td>
<td>c</td>
<td>850-900</td>
<td>ca. 45</td>
</tr>
</tbody>
</table>

150 g. of the reduced iron powders were added in an air-free state to 1 kg. of crude oil or heavy oil having a known sulfur content, they were agitated sufficiently for 1 hour at room temperature and allowed to settle. After 30 minutes, the precipitates were removed by filtration and the content of sulfur in the filtrate was measured. The results were as follows.

| Sample | After desulfurization by the reduced iron powders | Case, in which (α) was used | Case, in which (β) was used | Case, in which (γ) was used |
|---|---|---|---|
| Sample | S-content | (Desulfurization ratio) | S-content | (Desulfurization ratio) | S-content | (Desulfurization ratio) |
| Crude oil | 2.58 | 1.43 (45) | 1.61 (30) | 2.45 (5) |
| Heavy oil | 2.73 | 2.69 (44) | 2.65 (30) | 2.67 (2) |

From the above results, it was found that the result of the case of using reduced iron powders (γ) prepared by reducing non-porous ore (C) containing a small amount of alumina with reducing gas (c) containing a small amount of hydrogen show a low desulfurization ratio, indicating that the case was unsuitable for the process of this invention.

Example 2

By single-distilling 1 kg. of the crude oil in Example 1 there was obtained 700 g. of a fraction, of which the sulfur content was measured. Then, into 1 kg. of the same crude oil were added 150 g. of reduced iron powders (α) in Example 1, and they were stirred for 60 minutes as in Example 1. After letting them stand for 30 minutes, they were single-distilled again while stirring. The distillation was carried out by placing between the distillation still and a cooler a pipe filled with 150 g. of the reduced iron powders and glass fibers in such a manner that the crude oil could pass through the pipe in the vapor phase, and when 700 g. of the oil was distilled out, the sulfur content in 700 g. of the fraction was measured. In addition, the distillation was carried out at normal pressure up to 300° C. and after that it was done at reduced pressures. The results were as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfur content</th>
<th>(Desulfurization ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil</td>
<td>2.58</td>
<td></td>
</tr>
<tr>
<td>Fractions obtained by distilling without being contacted with the reduced iron</td>
<td>2.11 (18)</td>
<td></td>
</tr>
<tr>
<td>Distillation</td>
<td>1.74 (36)</td>
<td></td>
</tr>
</tbody>
</table>