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# METHOD OF TREATING METAL CONTAINING HYDROCARBON OILS

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The present invention relates to demetallization processes. In one of its aspects, the invention relates to a process for the demetallization of hydrocarbon oils. More particularly, in this aspect, the invention relates to an improved process for the removal of metal contaminants present in hydrocarbon oils, such as petroleum oils which are normally employed in catalytic cracking operations.

A major problem in conducting catalytic cracking operations of petroleum or other hydrocarbon oils, is the deactivation of the catalytic material employed. It has been found that this condition is largely due to the deposition of metallic contaminants, present in the feed, upon the catalytic material. These metallic contaminants which are harmful to catalytic activity have been found to comprise unfilterable metals or metallic compounds, particularly those of nickel, vanadium, iron and copper. In addition, it has also been found that organic metal salts are present in these hydrocarbon oils which may have been formed by the corrosion of refinery equipment by organic acids present in the feed. These metallic contaminants tend to accumulate upon the catalyst, and their removal is extremely difficult because of the relatively small amounts of the metal contaminants present in the feed, these amounts being in the order of from 10 to 100 parts per million.

Various methods have heretofore been suggested for removing or lowering the metallic contaminant-content of hydrocarbon oils or feed stocks, to reduce catalyst contamination. Among these methods are those which embody treating such feeds with strong mineral acids to react with the metal contaminants, and subsequently separating the resulting metal salts by conventional methods. Such procedures, however, have been found to result in hydrocarbon decomposition; and in instances where oxygenated organic compounds may also be present in the aforementioned feeds, there is a tendency for these compounds to react with the acid-treating agent, thus effecting their subsequent recovery in a state of unchanged composition. Other proposed methods embody treating the aforementioned metal-containing hydrocarbon oils with varying concentrations of alkali-treating agents. Such methods have also been found to be undesirable, inasmuch as they are limited to only a partial recovery of the metal contaminants present. This result is encountered where a sufficient amount of alkali-treating agent is used to neutralize the free organic acids which may be present in such metal-containing hydrocarbon mixtures, and it is desired to remove the metal as its oxide or hydroxide. Where such quantities of alkali-treating agent are employed, there is a tendency of the alkali to promote undesirable side-reactions, such as the condensation and/or polymerization of carbonyl compounds (e.g., aldehydes or ketones), unsaturated products, and materials containing polyfunctional groups. Such action is more apt to occur in the presence of alkali-treating agents



than in the presence of mineral acids, when the latter are employed as treating agents. Still other methods for removing dissolved metal impurities in admixture with hydrocarbons have been unsuccessfully attempted in the past. For example, distillation by conventional methods has proved undesirable because of hydrocarbon decomposition caused by the application of heat. Similarly, molecular distillation has been shown to be ineffective in separating metallic impurities from the aforementioned hydrocarbon oils.

It is, therefore, an object of the present invention to provide an improved method for the demetallization of hydrocarbon oils.

Another object of the invention is to provide an improved method for the removal of metal contaminants present in hydrocarbon oils, such as are employed in catalytic cracking operations.

Still another object of the invention is to provide an improved, efficient and economical method for substantially complete removal of metal contaminants present in hydrocarbon oils, such as are employed in catalytic cracking operations.

Various other objects and advantages inherent in the invention will become apparent from the following more detailed disclosure and description.

In accordance with the improved process of the present invention, as more fully hereinafter described, metal contaminants, present in varying concentrations, may be substantially completely removed from the aforementioned hydrocarbon oils by treating these oils with strong halogenating agents containing chlorine or bromine substitution, to convert these metal contaminants to their metallic halides. The metallic halides thus produced are thereafter readily separated from the hydrocarbon oil so that the metal-free hydrocarbon mixtures are obtained. The halogenating agent which is employed for the removal of the aforementioned metal contaminants, is, as indicated above, one in which the halogens are selected from the group consisting of chlorine and bromine. Preferred halogenating agents comprise sulfuryl chloride, sodium hypochlorite, chlorine, bromine or N-bromosuccimide.

The treatment of the aforementioned hydrocarbon oils, such as, for example, employed in catalytic cracking operations, is carried out with the halogenating agent in either a batch-wise or continuous operation. In a given treatment, it is found that the mole ratio of the halogenating agent to the quantity of metallic contaminants present in the feed stock treated, in general, may vary from about 1 to about 5 moles of chlorinating agent to the quantity of metal contaminants present. Greater quantities of the chlorinating agent with relationship to the quantity of metal contaminants present may, however, be employed in the process of the invention, but such increased quantities are not desirable since they do not result in any improvement in metal removal, from an economic standpoint. Preferably, mole ratios of halogenating agent to metal contaminants present ranging from about 1:1 to 3:1 are preferred, since such ratios result in obtaining optimum (i.e., substantially complete metal removal) conditions employing minimum quantities of the halogenating agent.

It has been found, in accordance with the process of the present invention, that the rate of chlorination or bromination is favored by an increase in temperature. However, if the temperature employed is excessive, too high a rate of halogenation takes place and too large a quantity of the halogenating agent is consumed. This may be followed by halogenation of the hydrocarbon

components themselves. In addition, there is also present the possibility of hydrocarbon decomposition where the temperature employed is exceedingly high. In general, temperatures between about 60° F. and about 300° F. are satisfactorily employed. While temperatures below 60° F. may also be employed, it is nevertheless found that the rate of reaction proceeds too slowly so that economic and efficient metal removal is not obtained. Where elevated temperatures are desired to be emloyed, in order to hasten the rate of metal removal, ranges between about 200° F. and about 300° F. are satisfactorily employed. In general operation, however, a temperature between about 60° F. and about 200° F. is normally utilized.

With respect to the aforementioned temperature ranges employed in carrying out the halogenation reaction, it is found that pressures between about 1 atmosphere and about 10 atmospheres are satisfactorily employed. In instances where the halogenating agent is employed in a liquid state and the operation is carried out within the uppermost limits of the temperature range (e.g., between about 200° F. and about 300° F.), it is preferred to carry out the reaction at pressures which are significantly above atmospheric pressure in order to maintain the halogenating agent in a liquid phase condition.

As previously indicated, the metal contaminants which are effectively removed, in accordance with the process of the present invention, comprise such metals as nickel, vanadium, iron, copper and their compounds. Employing nickel oxide as representative of metal contaminants present in the aforementioned hydrocarbon oils or petroleum feed stocks, the complete removal of this metal from the feed, employing sulfuryl chloride as representative of the aforementioned halogenating agent, may be illustrated by the following equation:

$$NiO+SO_2Cl_2 \rightarrow NiCl_2+SO_3$$

Similar reactions take place when any of the other metal contaminants are present in the feed, such as vanadium, iron, copper, etc., employing either sulfuryl chloride or any other of the other aforementioned halogenating agents.

As indicated above, the metal contaminants removed from the hydrocarbon oils, in accordance with the present invention, may be present either in the form of the elemental free metal or in the form of metallic compounds. In this respect, it has been found that in certain feed materials, particularly heavier crude oil fractions containing relatively large quantities of metal contaminants, such as nickel, vanadium, iron, copper or mixtures thereof, these metals are present in the form of metal porphyrins. These metal porphyrins, when present in feeds employed in hydrocarbon conversion processes, e.g., catalytic cracking operations, tend to deposit on the catalyst, as previously indicated, during cracking. With the above in mind, the effect of a number of halogenating agents for effecting demetallization of the aforementioned hydrocarbon oils was studied employing synthetic nickel and vanadyl porphyrin. Etioporphyrin I, which has been synthesized by Fischer and others, was complexed with nickel and vanadyl salts, in accordance with the procedure reported in a paper presented by Erdman, Ramsey and Kalenda, before the Division of Petroleum Chemistry, American Chemical Society, Dallas Meeting, April 8–13, 1956. Solutions of these complexes were then made and degradation of these complexes by treatment with various reagents was observed.

The following table illustrates the effect of various halogenating agents upon solutions containing nickel etioporphyrin. In each run a 10 cc. solution of nickel etioporphyrin, comprising 12.1 p.p.m. Ni in pyridine, was treated with the halogenating agent for a period of 16 hours. The data in the table discloses the quantities of halogenating agent employed and the degree of metal contaminant finally removed after the 16 hour period.

*Table I*

| Run No. | Halogenating Agent | Mg. of Halogenating Agent | Temp. | Final p.p.m. Ni | Percent Ni removed |
|---|---|---|---|---|---|
| 1 | sulfuryl chloride | {18.8<br>18.8 | room [1]<br>reflux [2] | 0<br>0 | 100.0<br>100.0 |
| 2 | sodium hypochlorite | 50.0 | reflux | 0 | 100.0 |
| 3 | chlorine ↑ | ---------- | room | 0 | 100.0 |
| 4 | bromine | 50.0 | reflux | 0 | 100.0 |
| 5 | N-bromosuccinimide | 22.0 | reflux | 0 | 100.0 |
| 6 | $S_2Cl_2$ | {30.9<br>30.9 | room<br>reflux | 8<br>8 | 34.0<br>34.0 |
| 7 | $SCl_2$ | {24.9<br>24.9 | room<br>reflux | 9<br>9 | 26.8<br>26.8 |
| 8 | $SOCl_2$ | {20.9<br>20.9 | room<br>reflux | 8.6<br>8.6 | 29.0<br>29.0 |
| 9 | HBr | 50.0 | reflux | 5.3 | 56.0 |
| 10 | $AlBr_3$ | 62.0 | reflux | 12.1 | 0 |

[1] Room temperature=68° F.
[2] Reflux temperature=reflux temperature of pyridine, viz., 221° F.

From Table I above, it will be noted that the halogenating agents of the present invention, viz., sulfuryl chloride, sodium hypochlorite, chlorine, bromine and N-bromo succinimide, were extremely effective in complete removal of the nickel contaminant present, as evidenced from the data in runs 1 through 5. On the other hand, it will be noted that other halogenating agents were not effective in the total removal of nickel contaminants, as is evidenced from runs 6 through 10 in the table.

The following table illustrates the effect of various halogenating agents upon solutions containing vanadyl etioporphyrin. In each run, a 10 cc. solution of vanadyl etioporphyrin, comprising 12.8 p.p.m. vanadium in benzene, was treated with the halogenating agent for a period of 15 hours. The data in the table discloses the quantities of halogenating agent employed and the degree of metal contaminant finally removed after the 15 hour period.

*Table II*

| Run No. | Halogenating Agent | Mg. of Halogenating Agent | Temp., F.° | Final p.p.m. V | Percent V removed |
|---|---|---|---|---|---|
| 1 | sulfuryl chloride | 50.0 | 68 | 0 | 100.0 |
| 2 | N-bromosuccinimide | 20.0 | 81 | 0 | 100.0 |
| 3 | HF | 50.0 | 81 | 12.8 | 0 |
| 4 | HI | 50.0 | 81 | 12.3 | 4.0 |
| 5 | HBr | 50.0 | 81 | 10.6 | 17.0 |

From the data disclosed in Tables I and II, it will be noted that the halogenating agents of the present invention, viz., sulfuryl chloride, sodium hypochlorite, chlorine, bromine and N-bromosuccinimide are outstandingly effective in obtaining substantially complete metal removal, by converting the aforementioned metal contaminants to their metallic halides. On the other hand, it will also be noted that other halogenating agents are not effective in obtaining a total metal removal as shown in the aforementioned runs. With reference to Table II, it will be noted therefore, that while the aforementioned halogenating agents of the present invention, as illustrated by sulfuryl chloride and N-bromosuccinimide, are effective in obtaining a substantially complete metal removal (as in runs 1 and 2), the other halogenating agents disclosed in Table II (as in runs 3, 4 and 5) were not effective in obtaining complete removal of the vanadium metal contaminants. The complete removal of vanadium from vanadyl etioporphyrin, employing sulfuryl chloride as representative of the aforementioned halogenating agents of the present invention, may be illustrated by the following equation:

$$V(\text{etioporphyrin})+5SO_2Cl_2 \rightarrow VCl_2+\text{etioporphyrin})Cl_3+5SO_2$$

As indicated above, the present invention is directed to an improved process for the removal of metal contaminants present in hydrocarbon oils, and has particu-

lar applicability to the treatment of hydrocarbon oils employed in catalytic cracking operations. However, while the invention has been described as having a particular applicability to the separation of metal impurities from hydrocarbon mixtures obtained from such sources, it should be noted that the process of the invention is not necessarily restricted to effect the desired metal separation from such hydrocarbon mixtures. The process of the present invention may also be successfully applied to the separation of metal impurities from any mixtures of hydrocarbon oils without regard to the source from which these mixtures may have been derived. It should also be noted that while a particular embodiment of the process of this invention has been described for the purposes of illustration, various modifications and adaptations thereof, which will be obvious to those skilled in the art may also be made within the spirit of the invention.

I claim:

1. A method for treating a hydrocarbon oil containing metal contaminants which comprises contacting said oil with a halogenating agent selected from the group consisting of sodium hypochlorite and N-bromosuccinimide to convert said metal contaminants to their metallic halides.

2. The process of claim 1 in which the halogenating agent comprises sodium hypochlorite.

3. The process of claim 1 in which the halogenating agent comprises N-bromosuccinimide.

4. A method for treating a hydrocarbon oil containing metal contaminants which comprises contacting said oil with a halogenating agent selected from the group consisting of sodium hypochlorite and N-bromosuccinimide at a temperature between about 60° F. and about 300° F. to convert said metal contaminants to their metallic halides.

5. A method for treating a hydrocarbon oil containing metal contaminants which comprises contacting said oil with a halogenating agent selected from the group consisting of sodium hypochlorite and N-bromosuccinimide at a temperature between about 200° F. and about 300° F. to convert said metal contaminants to their metallic halides.

6. A method for treating a hydrocarbon oil containing metal contaminants which comprises contacting said oil with a halogenating agent selected from the group consisting of sodium hypochlorite and N-bromosuccinimide at a temperature between about 60° F. and about 300° F. and at a pressure from about 1 atmosphere to about 10 atmospheres to convert said metal contaminants to their metallic halides.



7. A method for treating a hydrocarbon oil containing metal contaminants which comprises contacting said oil with a halogenating agent selected from the group consisting of sodium hypochlorite and N-bromosuccinimide at a temperature between about 200° F. and about 300° F. and at a pressure from about 1 atmosphere to about 10 atmospheres to convert said metal contaminants to their metallic halides.

8. A method for treating a hydrocarbon oil containing metal contaminants which comprises contacting said oil with a halogenating agent selected from the group consisting of sodium hypochlorite and N-bromosuccinimide in an agent:metal mole ratio between about 1 and about 5 and at a temperature between about 60° F. and about 300° F. to convert said metal contaminants to their metallic halides.

9. A method for treating a hydrocarbon oil containing metal contaminants which comprises contacting said oil with a halogenating agent selected from the group consisting of sodium hypochlorite and N-bromosuccinimide in an agent:metal mole ratio between about 1 and about 5 and at a temperature between about 200° F. and about 300° F. to convert said metal contaminants to their metallic halides.

10. The process of claim 6 in which the halogenating agent comprises sodium hypochlorite.

11. The process of claim 6 in which the halogenating agent comprises N-bromosuccinimide.

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