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DEMETALATION WITH CYANIDE ION

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ABSTRACT OF THE DISCLOSURE

A process for the removal of iron from iron-contaminated hydrocarbon oil by contacting the oil with a treating agent comprising an aqueous solution of cyanide ion. Iron may be selectively removed from an oil contaminated with nickel and vanadium as well as iron. A refinery foul water may be the source of the cyanide ion.

BACKGROUND OF THE INVENTION

This invention relates to the removal of metallic contaminants from hydrocarbon oils and, in particular, to the selective removal of iron therefrom.

In catalytic cracking, it has been known for some time that certain metals, particularly iron, nickel, and vanadium, are very harmful to cracking catalysts. When deposited on cracking catalysts in concentrations of about 0.1 percent or less, such metals cause the production of excessive amounts of coke and gas at the expense of valuable gasoline and heating oil fractions. This leads to an overloading of the regeneration and gas handling equipment and reduces the allowable feed rate to the catalytic cracking units. Iron has been found to be a particularly detrimental contaminant not only in catalytic cracking but in other catalytic processes, such as hydrocracking.

This iron is brought into a cracking unit along with the other unfilterable metallic impurities, most commonly nickel and vanadium, with the feedstock in the form of metallo-organic compounds. It is the removal of these iron contaminants with which the present invention is concerned.

SUMMARY OF THE INVENTION

The process of this invention is a process for the removal of iron from an iron-contaminated hydrocarbon oil which comprises contacting the oil with a treating agent comprising an aqueous solution containing cyanide ion. In another embodiment, the process is one for the selective removal of iron from a hydrocarbon oil contaminated with iron, nickel, and vanadium which comprises contacting the oil with a treating agent comprising an aqueous solution of cyanide ion.

DETAILED DESCRIPTION OF THE INVENTION

In its broadest form, the process of this invention is a process for the removal of iron from an iron-contaminated hydrocarbon oil which comprises contacting the oil with a treating agent comprising an aqueous solution containing cyanide ion. The contacting of the iron-contaminated oil and the treating agent may be accomplished in any number of ways. The oil and treating agent may be passed through a contacting chamber which may be filled with inert particles designed to promote liquid-liquid contacting and then through a settling tank. Alternatively, the oil and treating agent may be contacted in a batch contacting device, such as a stirred vessel. Many variations of either of these systems and many other types of contacting devices suitable for use in this process are known and will readily suggest themselves to those skilled in the art.

A wide range of reaction conditions may be used in this process. Temperatures may range from about 0°–300° F. A preferred temperature range is from 70°–200° F. with the most preferred operating temperatures at about 150° F. The freezing and boiling points of the aqueous solution of cyanide ion will essentially determine the outer limits of the temperature range which can be employed. Where high pressures are used, reaction temperature may range above 300° F. as long as the pressure used is sufficient to maintain all constituents in the liquid phase. Pressures may range from atmospheric to 2,500 p.s.i.g. or greater. It is most convenient to use pressures of approximately 0–100 p.s.i.g. At these pressures and at moderate temperatures substantial iron removal can be accomplished without the necessity of employing expensive or cumbersome high pressure reaction equipment. Contacting times, which in a flow system will be a function of the space velocity of the reactants through the contacting vessel, should be sufficiently long to insure that all the iron-containing compounds will be properly contacted by the cyanide ion. In general, satisfactory contacting times can be from one minute to two hours or more. The optimum contacting time for any given feed will depend on the degree of iron-contamination of the oil, the reaction temperature, the ratio of oil to treating agent, and the concentration of cyanide ion in the treating agent. At higher temperatures and with higher volumes of treating agents and concentrations of cyanide ion, the contacting times will be shorter. Conversely, at lower temperatures or with less treating agent or cyanide ion, contacting times will have to be longer in order to obtain the maximum iron removal. Determination of the optimum conditions for any given batch of oil within these ranges can readily be determined by one skilled in the art.

A wide variety of oils may be treated by this process. In general, these will be higher boiling oils, such as crude oils, deasphalted oils, shale oils, residua, topped crudes, and similar materials which contain iron contaminants. It is often desirable to subject the oil to some sort of fractionation process prior to iron removal in order to separate the lower boiling constituents of the oil. Since essentially all iron-containing, organic compounds are high molecular weight, high boiling materials, it is apparent that these will be found among high boiling oils. Thus removal by distillation or some other separation process of the low boiling oils reduces the amount of material which must be treated in this process without substantially reducing the total iron removal since the iron will be concentrated in the high boiling materials. In some cases, as where the oil to be contacted is especially heavy and viscous, it may be desirable to have some light solvent present to facilitate the contacting of the oil and treating agent. Typical such solvents are light paraffins and light aromatics, such as propane, pentane or xylene.

The treating agents used in the process of this invention are aqueous solutions containing cyanide ion. These may be simple aqueous solutions of an ionic cyanide salt, such as sodium cyanide. They may also be aqueous solutions containing numerous other ions along with the cyanide ion, such as carbonate ions or halide ions. Dissolved materials, such as gases, may also be present as long as their presence (and the presence of the extraneous ions mentioned in the preceding sentence) does not substantially affect the efficacy of the cyanide ion. One such treating agent which is readily available in oil refineries is the so-called foul water stream which is collected from various stripping units and other re-

finery apparatus in which gases, such as ammonia and H_2S, are separated from the hydrocarbon effluents of refinery processes, such as catalytic cracking, hydrogen processing, and denitrification or desulfurization. Such foul water streams contain cyanide ion, ammonia, hydrogen sulfide, and various other contaminants and are generally considered waste products to be disposed of in some manner. By utilizing such a stream in the process of this invention, a hitherto waste stream with a negative economic value is converted into a valuable reactant. The solvent referred to in the preceding paragraph may be introduced as a component of the treating agent rather than with the oil, if desired.

Cyanide ion concentration in any kind of aqueous solution may range from about 50 parts per million to about 2 percent by weight. If the concentration of cyanide ion is too low, temperature will have to be too high and contacting time too long for the process to be practical. Further, if the cyanide ion concentration is too low, operation at practical reaction conditions will produce only a reduced amount of iron removal. On the other hand, increasing the cyanide ion level beyond a concentration of 1 or 2 percent by weight will product essentially no additional iron removal and may cause corrosion or handling problems in the system. Further, at the higher cyanide ion levels, some degree of vanadium and nickel removal will occur. The preferred range of cyanide ion concentration is between 100 and 2,000 p.p.m. The cyanide ion must be present in an amount at least equal to the stoichiometric amount necessary to convert all the iron present. However, if sulfide ion is also present, adidtional cyanide ion must be used.

The data in the following table illustrate this process. In the runs illustrated in this table, iron-contaminated, deasphalted oils where contacted with various types of aqueous cyanide solutions under different conditions of temperature and pressure. Iron contents of the feed oils varied from 6 to 24 p.p.m. iron. Nickel and vanadium in amounts from 10 to 50 and 4 to 21 p.p.m., respectively, were also present.

TABLE

	Run					
	A	B	C	D	E	F
Treating agent, p.p.m.:						
Type	(1)	(1)	(2)	(3)	(1)	(1)
Initial CN- content	126	162	1,000	2,600	162	162
Added CN-	0	0	0	0	540	500
Total CN- content	162	162	1,000	2,600	702	662
Volumetric analysis, cc.:						
Oil	150	150	175	35	150	170
Xylene diluent	300	300	345	265	300	340
Treating agent	150	150	300	300	150	305
Treating conditions:						
Temperature, ° F	90	167	195	400	149	196
Pressure, p.s.i.g	0	0	0	2,300	0	0
Contacting time, min	15	15	16	30	5	15
Metals removal, percent removal of:						
Iron	62	86	86	67	91	96
Nickel	6	<1	<1	12	<1	<1
Vanadium	<1	<1	<1	9	<1	<1

[1] Feul water.
[2] NaCN solution.
[3] NaCN solution, also contains hydrogen dissolved in solution.

It will be apparent from the above Table that over a wide range of contacting temperatures and pressures and with varying amounts of cyanide ion and varying ratios of volumes of treating agent per volume of oil, there was a high degree of removal of iron from the contaminated oil, although at the same time essentially no removal of nickel and vanadium until the cyanide ion concentration became extremely high. This property of selective iron removal will be especially useful in instances where a particular oil has an iron content disproportionately high compared to its content of other metals, so that iron removal will constitute the major part of any demetalation process.

The above examples and data are given for illustrative purposes only and are not meant to limit the scope of the process of this invention. It is apparent that many variations and specific embodiments of this process will immediately suggest themselves to those skilled in the art, and it is intended that these be included in the scope of the process of this invention. Therefore, that scope is not meant to be limited except as defined in the appended claims.

We claim:

1. A process for removing iron, present as a soluble organo-metallic compound, from a hydrocarbon feedstock of the group consisting of crude oils, deasphalted oils, shale oils, residua and topped crude oils which comprises contacting the hydrocarbon feedstock at a temperature between 0–300° F. and a pressure between atmospheric and 2500 p.s.i.g., with an aqueous solution containing cyanide ion.

2. A process for the selective removal of iron, present as a soluble organo-metallic compound, from a hydrocarbon oil contaminated with iron, nickel and vanadium which comprises contacting the hydrocarbon feedstock at a temperature between 0–300° F. and a pressure between atmospheric and 2500 p.s.i.g., with an aqueous solution containing cyanide ion.

3. The process as defined in claim 1 wherein the concentration of said cyanide ion in said aqueous solution is in the range of from about 50 parts per million to about 2 percent by weight.

4. The process as defined in claim 3 wherein the concentration of said cyanide ion in said aqueous solution is in the range of from about 100 to about 2,000 parts per million.

5. The process as defined in claim 1 wherein said aqueous solution comprises a refinery foul water stream.

6. The process as defined in claim 1 wherein the amount of iron in the oil product totals less than 40 percent of the iron originally in the feed to said process.

7. The process of claim 1 wherein said reaction temperature is in the range of 70° to 200° F. and said reaction pressure is in the range of 0 to 100 p.s.i.g.

8. A process in accordance with claim 1 wherein the aqueous solution contains H_2S and NH_3 in addition to the cyanide ion.

9. A process in accordance with claim 8 wherein the aqueous solution is a foul water stream derived from a catalystic cracking process.

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