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FOULING RATE REDUCTION IN HYDROCARBON STREAMS

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ABSTRACT OF THE DISCLOSURE

Fouling accompanying the treatment of hydrocarbon streams at elevated temperatures is reduced by contacting the hydrocarbons in the presence of hydrogen and antifouling compositions containing one or more of detergents, dispersants, metal deactivators, corrosion inhibitors and antioxidants.

This application is a continuation-in-part of my copending application Ser. No. 62,718, filed Aug. 10, 1970, now abandoned.

BACKGROUND OF THE INVENTION

The numerous processes involved in modifying the physical and chemical properties of hydrocarbon oils such as reforming, hydroforming, absorption, hydrocracking, isomerization, extraction, cracking, fractionation, hydrofining, thermal desalting and the like, almost without exception necessitate exposure of the hydrocarbon feed to relatively elevated temperatures. These temperatures are most commonly attained by the use of heat exchangers in which the hydrocarbon feeds, products or intermediates are intimately contacted with heat exchange surfaces. These conditions are known to promote the formation of fouling deposits which can drastically limit heat exchange capacities and flow rates. Several of the areas in which this problem was first observed include preheat exchangers of crude units, hydrodesulfurizers and fluid catalytic cracking systems. Other problem areas include overhead condensers, reformer reboilers, coker furnaces, vacuum tower and alkylation reboilers and the like.

Although the problems associated with fouling deposit formation are probably most acute in the hydrocarbon processing industry, they are by no means limited to those systems. For example, difficulties associated with foulant deposition have also been recognized in petrochemical processes involving ethylene, styrene, butadiene, isoprene, acrylonitrile and other chemicals.

The problem associated with equipment fouling is well recognized in the art as pointed out by Guthrie in "Petroleum Products" (McGraw-Hill, 1960), pp. 1–13. It is also generally recognized that these problems are not necessarily limited to heat exchange apparatus as such. On the contrary, the formation of fouling deposits accompanying the thermally initiated physical or chemical modification of hydrocarbons is observed almost any time a hydrocarbon phase is exposed to a retaining surface, metallic or otherwise, at elevated temperatures in process equipment such as fractionating columns, reactors, intermediate piping, heat exchange equipment and the like. Deposits of this nature are known to materially decrease heat transfer characteristics of the effected systems and are generally removed only with considerable difficulty. The consequent increases in operating and maintenance expense accompanying the formation of such deposits is often substantial. Consequently, considerable effort has already been devoted to the solution of these problems with the result that numerous alternative procedures have been proposed for either preventing foulant deposition or removing fouling deposits. These alternatives have met with varying degrees of success.

The fouling deposits which are encountered as a result of the physical and/or chemical modification in the hydrocarbon feed initiated by elevated process temperatures may consist of sticky, tarry, polymeric or carbonaceous material. The most common fouling deposits can be generally classified as inorganic salts, corrosion products (metallic oxides and sulfides), metal-organic compounds, organic polymers and coke. The inorganic salts such as sodium, calcium and magnesium chloride are probably carried into the process system with the crude feedstock. The metal-organic compounds may also be present in the original feed or may be formed on heat transfer surfaces by combination with corrosion products or other metals carried into the system. The formation of organic polymers is most commonly attributed to reaction of unsaturated hydrocarbons. However, polymers can also be formed by the reaction of nitrogen and sulfur containing organic compounds which are believed to polymerize via a mechanism involving oxygen, usually in the presence of a metal catalyst. It has been suggested that these metal catalysts may be either corrosion products, i.e., sulfurization or oxidation products, metal-organic compounds or free metal, either carried into the system with the process stream or available on the interior surfaces of processing equipment. Coke deposition is usually associated with the occurrence of hot spots caused by the accumulation of other fouling deposits. Consequently, it can be seen that the metal and organic elements of these fouling deposits interact and influence each other. Thus, any effort to completely control or eliminate fouling should involve the elimination of both the organic polymers and the metal contaminants related to corrosion.

My experience to date and results made available by other investigators have indicated that fouling deposits may have organic contents as high as 95%. However, such deposits typically contain much higher proportions of inorganic substances usually bound together with an organic polymeric or tarry matrix. For example, a typical deposit isolated during the course of these investigations contained 2 weight-percent silica, 38 weight-percent Fe_2O_3, 1% alumina, 18% sulfur determined as SO_3 and 41% organic material determined by loss on ignition. The nature of such deposits leads one to the conclusion that fouling results from a rather complex process involving the occurrence of many reactions.

The inorganic constituents of these fouling deposits may be present due to lack of adequate filtering of the hydrocarbon, e.g., crude or topped crude feed, while the scale deposits generally result from deterioration, i.e., corrosion, of the process equipment. The inorganic salts are most commonly derived from crude oils which have not been sufficiently desalted prior to processing. However, in some instances, e.g., in the operation of pipe stills, it has been found most expeditious to bypass desalination if the salt content of the crude stock does not exceed 20 pounds per 1000 barrels. The presence of these inorganic salt and scale components, although undesirable, does not of itself impose a substantial burden on any given process. However, when combined with the tarry or carbonaceous organic foulants, these materials contribute to the formation of tenacious deposits which can be removed only with considerable difficulty.

Several of the approaches taken to minimize these effects involve polishing or coating of process equipment in an effort to reduce its affinity for fouling materials. However, it is practically impossible to prevent the formation of these deposits by coating the metal surfaces with protective permanent coating without a consequent loss of process efficiency due to the inescapable loss of heat transfer capacity attributable to the coating itself. Nevertheless, such procedures are definitely beneficial in many instances.

Yet another alternative which does not necessitate the expense involved in process equipment coating and does not result in the accompanying loss in heat transfer capacity involves the addition of chemical constituents to the hydrocarbon feed which act to either prevent the formation of foulant material or to prevent its adhesion to process equipment. Numerous compositions each of which serve to perform one or more desirable functions have been devised for the purpose of preventing or mitigating the effects of fouling deposit formation in process systems. Usually these compositions are designed to operate as either metal deactivators, corrosion inhibitors, detergents, dispersants or antioxidants. In addition, it is also advantageous to formulate compositions that perform more than one of these functions at the same time in order to combat a plurality of undesirable effects.

Corrosion inhibitors suitable for these purposes have been discussed in detail by previous investigators such as, Bregman in his book Corrosion Inhibitors, MacMillan Company, New York, Collier-MacMillan Ltd., London, 1963. Exemplary of conventional corrosion inhibitors are mono- and polyamines, mono- and polyamides and polyethoxylated amines having about 5 to about 200 carbon atoms per molecule, and the salts of organic and inorganic acids such as acetic, oleic, dimeric, naphthenic, and phosphoric acids. This class of compounds is intended to include polyfunctional amphoteric compounds such as aminocarboxylic acids containing dissimilar functional groups, e.g., amino and carboxylate linkages. The most common corrosion inhibiting compositions employed in such applications are the relatively high molecular weight amines preferably the cyclic or endocyclic secondary amines having 3 to 5 carbon atoms per ring, about 18 to about 50 carbon atoms and 1 to about 3 amino groups per molecule similar to those described in connection with the detergent-dispersant compositions, infra. The alkyl and/or amino alkyl substituted and unsubstituted imidazolines, amines and aliphatic acid salts having 5 to 50 carbon atoms are illustrative of compounds within this class having effectiveness as corrosion inhibitors. These compositions are usually employed in concentrations within a range of 1 to about 1000 p.p.m.

Several metal deactivators have found considerable commercial success exemplary of which are N,N'-disalicylidene-1, 2-diaminopropane marketed by Ethyl Corporation as "Ethyl" metal deactivator and N,N'-disalicylidene-1, 2-propanediamine in an organic solvent marketed as "DMD" by Du Pont. The metal deactivators are usually employed to complex or otherwise inhibit the chemical activity of metals originally present in hydrocarbon streams or picked up by contact with processing equipment. As a general rule very minor concentrations of these deactivators are effective for accomplishing the prescribed purpose. These concentrations are usually within the range of about 0.1 to about 1000 p.p.m. based on total hydrocarbon.

A number of detergent compositions have found varying degrees of commercial acceptance. These compositions also often serve as dispersants when such functionability is desired.

Exemplary of effective detergents, which are generally exhibit dispersant properties are the sulfonates, usually including the normal and basic metal salts of petroleum sulfonic (mahogany) and long chain alkyl substituted benzene sulfonic acids usually having about 8 to about 100 carbon atoms and up to about 5 sulfonic acid or sulfonate groups per molecule; phosphonates and/or thiophosphonates, including the normal and basic salts of the phosphonic and/or thiophosphonic acids obtained from the reaction of polyolefins such as polyisobutenes with inorganic phosphorus agents, principally phosphorus pentasulfide; phenates including the normal and basic metal salts of alkylphenols, alkylphenol sulfides, and alkylphenol-aldehyde condensation products usually having up to about 20 carbon atoms per molecule; alkyl substituted salicylates including the normal and basic metal salts, especially the carboxylate and carboxylate-phenate salts, of long chain alkyl substituted salicylic acids; alkenyl succinimides having about 20 to about 200 carbon atoms per molecule, alkali metal naphthenates having about 10 to about 30 carbon atoms; and primary and secondary amines and carboxylic acids generally having about 10 to about 50 carbon atoms and up to about 4 amino groups. The most effective high molecular weight amines presently employed to any substantial degree are the endocyclic five and six membered substituted heterocyclic amines such as an imidazoline.

One or more of these detergent-dispersant compositions can be employed in combination in any given application. Very minor concentrations of these constituents are effective in somewhat reducing the degree of foulant deposit accumulation. They are generally employed in concentrations within a range of about 1 to about 1000 p.p.m.

Currently, the most popular oxidation inhibitors are those formulated with the view of producing a composition having the ability to reduce organic peroxide concentration in a hydrocarbon process stream thereby interrupting chain oxidation reactions. Effective concentrations vary considerably, but are usually between about 1 and 1000 p.p.m. Exemplary of effective antioxidants are the hydrocarbyl sulfides, disulfides, sulfoxides, phosphites, mono- and poly-acyclic and cyclic amines such as the condensation products of cyclohexylamine or aromatic diamines with catechol, its alkaline derivatives and/or alkyl phenols, substituted and unsubstituted phenols, selenides and zinc dithiophosphates. Similar compositions are described in more detail in U.S. Pat. 3,342,723. Antioxidant compositions also often contain compounds possessing one or more of these functional groups such as N,N'-di-sec-butyl - p - phenylenediamine, N,N'-butyl-p-aminophenol, 2,6-di-t-butyl-p-cresol and the like.

As mentioned above, fouling inhibitor compositions are often formulated with the view of preventing or inhibiting one or more undesirable fouling reactions. Hence, these additives often contain poly-functional compounds or one or more compounds having dissimilar functional groups. Exemplary of commercially available poly-functional additives are Polyflo 135 and 140 marketed by Universal Oil Products. Polyflo 135 is believed to comprise alkyl substituted ethoxylated catechol and a corrosion inhibitor comprising a long chain dimeric aliphatic acid and a primary amine. Polyflo 140 is believed to comprise a polyhydroxy ethoxylated amine. These compositions are described in more detail in U.S. Pat. No. 3,062,-744 incorporated herein by reference. Another composition marketed as a fouling inhhibitor is Betz AF–104 marketed by Betz Laboratories of Philadelphia, Pa. This composition is believed to comprise a metal deactivator similar to those above described, a bifunctional phenolic amine and an alkyl substituted succinimide. Succinimides of this nature are described in U.S. Pat. 3,380,909. Similar compositions are discussed in more detail in U.S. Pats. 3,271,295, 3,271,296 and 3,437,583 incorporated herein by reference.

Nalco 261, available from Nalco Chemical Company, is also a commercially available fouling inhibitor and is believed to contain morpholine and a water soluble salt of ethoxylated imidazoline. Similar compositions are discussed more comprehensively in U.S. Pats. 3,105,810, 3,261,774 and 3,224,957 incorporated herein by reference. Tretolite Aftol–21, designated primarily for the prevention of fouling in process heat exchange equipment, is marketed by the Petrolite Corporation and is believed to consist primarily of succinimides.

It should be observed that the exact composition of these formulations is not generally made public by the manufacturers of the respective compositions and can be at best only approximated analytically by considerable

effort. Nevertheless, the presence of certain functional groups can be established with relatively certainty and to a degree sufficient to illustrate the effectiveness of the compositions of this invention relative to previously described compositions. In addition, these compositions and information regarding their use are of course available from the respective manufacturers noted above.

Unfortunately none of the expedients intended to reduce deposit formation thus far developed are successful in completely eliminating this source of difficulty in hydrocarbon processing. Consequently, efforts are continuing to effect even greater improvement in both the physical and chemical systems involved in these operations to minimize, if not completely eliminate, fouling deposit formation. Toward this end I have discovered that substantial reduction in the rate of fouling deposit formation and accumulation can be realized by contacting the selected hydrocarbon stream in the presence of hydrogen and an antifoulant containing one or more of detergents, dispersants, metal deactivators, corrosion inhibitors and antioxidants.

It is therefore one object of this invention to provide a method for reducing the formation of fouling deposits in hydrocarbon process systems. Yet another object of this invention is to prevent or at least minimize the formation of fouling deposits in hydrocarbon processing equipment. Another object of this invention is the reduction of fouling deposit formation upon contact of hydrocarbon media with heat exchange surfaces.

In accordance with one embodiment of this invention the rate of fouling deposit formation and accumulation in hydrocarbon processing equipment is substantially reduced by contacting the hydrocarbons in the presence of hydrogen and an antifoulant composition comprising one or more of detergents, dispersants, metal deactivators, corrosion inhibitors and antioxidants.

The antifoulant compositions of this invention can be employed in combination with essentially any hydrocarbon process stream including light distillates, e.g., naphthas, kerosenes and the like, middle distillate stocks from cracking operations, virgin crude oils, topped crude oils, and the like. The great majority of hydrocarbon streams usually employed in such processes boil above about 200° F. The greatest degree of improvement in fouling rate is observed with these procedures when operating on finished or semifinished hydrocarbons such as the hydrotreated or more highly refined crude stocks.

The most severe fouling problems are usually associated with higher boiling stocks, particularly those containing a substantial portion of unsaturated hydrocarbons boiling between about 400 and 1300° F. Hydrocarbon mixtures which generally exhibit the greatest propensity for producing foulant deposits are those containing unsaturated hydrocarbons, e.g., olefins and aromatics, usually in amounts of at least about 5 volume percent and generally in excess of 15 volume percent. Olefin concentrations are generally in excess of about 5 volume percent.

The fouling problem associated with these hydrocarbon mixtures is generally promoted at elevated temperatures. The mechanisms are believed to involve polymerization or a combination of polymerization and oxidation which, in some respects, are similar to the mechanisms leading to gum formation in gasolines. The high temperatures attained in heat transfer or other process steps are believed to promote the combination of hydrocarbons with oxygen to form a polymeric material that may deposit on the surfaces of process equipment, particularly in heat transfer areas.

Although fouling promoted by these mechanisms, i.e., oxidative polymerization and the like, might be controlled by excluding oxygen from the process, that objective cannot always be economically achieved. For example, the ordinary floating roof tanks in which feedstocks are frequently stored are not completely effective in preventing contact of the hydrocarbon with atmospheric oxygen. Furthermore, many feedstocks contain oxygen as they are received at a refinery or at a process site. Consequently, the utilization of other alternatives for the prevention of foulant formation such as the antifoulant compositions of this invention are often necessary.

It is presently believed that these antifoulant compositions operate in one or two ways or a combination of both to effect reduction of foulant deposits. They may either prevent the formation of organic polymers or highly condensed polynuclear aromatic carbonaceous deposits by interfering with the chemical mechanisms necessary to the formation of such materials or they may reduce the affinity of such substances once formed for available surfaces.

I have now found that the rate of fouling formation and deposition can be dramatically reduced by combining with the hydrocarbon phase an antifoulant composition having the ability to inhibit the several mechanisms contributing to foulant deposit formation in the presence of elemental hydrogen. This observation was quite surprising in view of the fact that the fouling rate of a given hydrocarbon stream was observed to be much higher in the presence of elemental hydrogen alone than was the case in the absence of the hydrogen. Although the rate of fouling deposit formation and deposition was observed to be substantially reduced in the presence of the detergents, dispersants, metal deactivators, corrosion inhibitors and antioxidants hereinafter detailed, it was not expected that the beneficial qualities of those compositions would be markedly improved by the addition of elemental hydrogen which otherwise contributes to the accumulation of foulant materials. Nevertheless, I have observed that when both the chemically active antifoulant compositions and elemental hydrogen are used in combination, and apparently synergistic affect is realized which renders the total composition much more effective than is the case in the absence of hydrogen.

Hydrogen concentrations effective for these purposes are usually in excess of about 1 p.p.m. based on total hydrocarbon phase. However, it is presently preferred that the hydrogen content of the hydrocarbon phase be determined with relation to the solubility of hydrogen at the conditions of temperature and pressure at which the hydrocarbon mixture is to be treated. On this basis, it is preferred that the hydrogen concentration be within the range of about 50 to about 100% of the saturation limit and even more preferably at the saturation limit. In any event, hydrogen levels in excess of 1000 p.p.m., or about 100 scf./bbl., are not required. Usual levels correspond to less than 100 p.p.m., or, preferably the saturation limit at standard conditions of temperature and pressure of about 2 to 8 p.p.m.

Due to the nature of the mechanisms involved in the formation of fouling deposits the problem is usually observed at temperatures in excess of about 250° F., generally within a range of about 350 to about 850° F. Temperatures substantially above this upper limit usually result in the occurrence of some thermal cracking which is generally undesirable and obviously contributes to the formation of carbonaceous deposits.

The advantages of these procedures are most apparent when the hydrocarbon stream is contacted with a heat exchange surface maintained at relatively high temperature. It is under these conditions that deposit formation usually results in the highest pressure drop and accordingly is the most problematical. Consequently, these methods can be employed to reduce fouling rates in processes not usually involving hydrogen or hydrogenative conversion. In fact, it is always preferable to assure that essentially no conversion such as cracking, hydrocracking or related reactions occur in heat exchange equipment.

The presently preferred mode of operation involves determining the hydrogen level, if any, in the hydrocarbon stream passed to the heat exchange zone and establishing whether or not that level corresponds to the desired

hydrogen concentration. Additional hydrogen is introduced if the inlet level is not within the desired range. It is also presently preferred that the antifoulant be admixed with hydrocarbon upstream of the heat exchange zone so that intimate admixture of the hydrocarbon, antifoulants and hydrogen can be achieved. By virtue of this arrangement both the antifoulant additives and hydrogen concentrations can be maintained at the desired predetermined levels. It is often the case that the feed to the heat exchange zone will contain no hydrogen whatever, or less than the amount desired. In such instances hydrogen will be added to the process stream either before or within the exchanger.

The following examples are presented to illustrate the effectiveness of the described procedures and should not be construed as limiting thereof.

EXAMPLES

The following examples were run sequentially with different fouling inhibitors and inhibitor concentrations in a two-stage preheater.

The two preheater stages were operated in series at 250 p.s.i.g. The first heater operated across a temperature range of 75° F. to 425° F. and an outlet temperature of 600° F. Each heater constituted an elongate tubular shell and an axially disposed resistive heater defining an annular cross section for the passage of the process stream. This apparatus was a modification of the Erdco coker originally developed to test the thermal stability of aviation turbine fuels in accordance with ASTM D–1660. The ASTM apparatus usually employs aluminum tubes and filters upstream and downstream of the apparatus. In order to obtain more adequate discrimination between these several fouling inhibitors the ASTM Erdco coker apparatus was modified by removal of the filtering system and substitution of a carbon steel tube for the original interior aluminum tube surrounding the resistive heater. The substitute carbon steel tube was of the same dimensions as the original aluminum apparatus and could be removed for weighing to determine the amount of weight gained during a specified period of operation. As already mentioned, a further modification included the use of two of these Erdco coker tubes in series to more closely simulate the operation of series heat exchangers at different temperature levels.

During each run the fouling inhibitors were injected into the hydrocarbon stream upstream of the first heating stage and the hydrocarbon-additive admixture was continuously passed through the series heaters at a rate of 4.5 pounds/per hour corresponding to a linear flow rate of .07 feet per second through each heater. Each run was continued for 90 minutes at the conditions and with the compositions illustrated in the table. The heat exchange tubes were weighed before and after each period of operation to determine the weight gain attributable to fouling deposit formation.

EXAMPLES 1–4

The additive employed in these examples was Nalco 261 described above. The hydrocarbon feed of this example boiled between 307 and 701° F. and contained 30 volume-percent aromatics, 1% olefins and 69% saturates and had an API gravity of 33.50 at 60° F.

TABLE 1

Example	Chemical	Weight gain of tubes, grams: 75/425° F. tube	Weight gain of tubes, grams: 425/600° F. tube
1	None	[1] 0.0071	[1] 0.0619
2	None—H_2 saturated [2]	[1] 0.2519	[1] 0.3349
3	10 p.p.m. Nalco 261	0.0042	0.0117
4	10 p.p.m. Nalco 261—H_2 saturated [2]	0.0016	0.0088

[1] Average of two series operations of 90 minutes each.
[2] At a temperature of 75° F. and atmospheric pressure.

From these data it is readily apparent that the addition of sufficient hydrogen to the hydrocarbon stream to saturate the hydrocarbon phase in the absence of the chemical inhibitor combination drastically increased the rate of foulant accumulation in both the 75/425° F. and 425/600° F. tubes. In the absence of hydrogen and in the presence of 10 p.p.m. Nalco 261 foulant inhibitor the foulant accumulation rate in the first, low temperature tube was slightly in excess of half of that observed in the absence of any inhibitor whatever and was less than 20% of that observed in the high temperature tube in the absence of inhibitor. The results of Example 4 employing the combination of 10 p.p.m. Nalco 261 with the hydrogen saturated hydrocarbon system evidenced that this combination dramatically reduced the fouling rate in both tubes below that observed with the chemical inhibitor alone as demonstrated in Example 3. This observation was rather unexpected in view of the markedly inferior results attributable to hydrogen as demonstrated in Example 2.

EXAMPLES 5–8

These investigations covered the use of yet another inhibitor composition. The feed of this example was a blend of 16 volume-percent cracked naphtha and 80 percent straight run gasoline boiling between 240 and 680° F. having an API gravity of 31.5 at 60° F. The results of these investigations are reported in Table 2.

TABLE 2

Example	Chemical	Weight gain of tubes, grams: 75/425° F. tube	Weight gain of tubes, grams: 425/600° F. tube
5	None	0.0166	0.0593
6	None—H_2 saturated [2]	0.0213	0.0965
7	20 p.p.m. Tretolite Aftol 21	0.0058	0.0615
8	20 p.p.m. Tretolite Aftol 21—H_2 saturated	0.0027	0.0565

[1] Average of two series operations of 90 minutes each.
[2] Saturated at 75° F. and atmospheric pressure.

Once again it was apparent that hydrogen markedly increased the fouling rate in both the low and high temperature tubes, although the degree of this increase was not nearly as high as that observed in Examples 1–4. Nevertheless, the fouling rate was markedly reduced in the presence of the chemical additive as illustrated in Example 7 wherein the hydrocarbon stream contained 20 p.p.m. of Tretolite Aftol-21. In a manner similar to that observed in Examples 1 through 4 the combination of hydrogen and the chemical additive reduced the fouling rate even further in both tubes as shown in Example 8. The fouling rate in the low temperature tube in Example 8 had been reduced to approximately 50% of that observed in Example 7. Although the fouling rate reduction in the high temperature, 425/600° F. tube of Example 8 was not as great as that observed in the first, low temperature tube, it was nevertheless substantial.

I claim:

1. A method of reducing the fouling rate in a heat exchange zone containing foulant-producing hydrocarbons boiling above about 200° F. upon contact with said heat exchange zone at a temperature above about 250° F. sufficient to cause fouling deposit formation in the absence of a foulant inhibitor which comprises adding to said hydrocarbon (a) an amount of hydrogen sufficient to provide a hydrogen concentration of at least about 1 p.p.m. and not greater than about 100 s.c.f./bbl. of said hydrocarbon, and (b) a foulant inhibiting amount of at least about 1 p.p.m. of a foulant inhibitor selected from substituted and unsubstituted cyclic, acyclic and endocyclic mono- and poly amines and amides having up to about 50 carbon atoms.

2. The method of claim **1** wherein said inhibitor is an endocyclic amine or amide and is added to said hydrocarbon in an amount of at least about 1 p.p.m. and not greater than about 1000 p.p.m., and said hydrogen con-

centration is at least about 1 p.p.m. and not greater than about 1000 p.p.m.

3. The method of claim 2 wherein said hydrogen concentration is within the range of about 1 to about 8 p.p.m.

4. The method of claim 1 wherein said inhibitor is selected from substituted and unsubstituted morpholine, imidazolines, and succinimides.

5. The method of claim 1 wherein said hydrocarbon boils substantially within a range of about 400 to about 1200° F. and contains at least about 15 volume percent of unsaturated constituents selected from aromatic and olefinic hydrocarbons and at least about 5 volume percent of olefinic hydrocarbons and the concentration of said hydrogen is controlled at a level within the range of about 1 to about 1000 p.p.m. by the addition of hydrogen thereto as required upstream of said heat exchange zone.

6. The method of claim 1 wherein said hydrocarbon boils primarily between about 400 and about 1200° F. and contains less than about 1 p.p.m elemental hydrogen upstream of said heat exchange zone, and sufficient hydrogen is added to said hydrocarbon prior to contacting in said heat exchange zone to maintain a predetermined hydrogen concentration within the range of about 1 to about 1000 p.p.m.

7. The method of claim 1 wherein said inhibitor is selected from (a) endocyclic amines and amides having 3 to about 5 carbon atoms in the ring structure and (b) the condensation products of (1) cyclohexylamines and aromatic mono and diamines having about 6 to about 20 carbon atoms and (2) alkyl substituted and unsubstituted phenols having about 6 to about 20 carbon atoms.

8. The method of claim 7 wherein said inhibitor is selected from (a) alkyl and aminoalkyl substituted and unsubstituted imidazolines having 3 to about 50 carbon atoms and (b) the condensation products of (1) cyclohexylamines or aromatic diamines with catechol or alkyl phenols having about 7 to about 20 carbon atoms.

9. The method of claim 6 wherein said hydrocarbon is contacted at a temperature of about 75 to about 600° F. and said inhibitor comprises morpholine and a water soluble salt of an ethoxylated imidazoline.

10. The method of claim 6 wherein said hydrocarbon is contacted at a temperature of about 75 to about 425° F. and said inhibitor is selected from succinimides having about 20 to about 200 carbon atoms.

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