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TREATMENT OF HYDROCARBON OILS

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This invention relates to the prevention, inhibition and restriction of the corrosion of metals. More specifically this invention relates to the restriction or prevention of corrosion when such action involves metals subject to corrosion in contact with refined hydrocarbon fluids and especially when also in contact with water, aqueous solutions or other aqueous material.

In the petroleum industry huge losses are suffered due to the internal corrosion of ferrous and other metal facilities for the handling, transportation and storage of refined hydrocarbon oils, liquefied gases and natural gas. Especially is this true of pipelines used to transport said fluids and the tanks in which the fluids are stored. Serious corrosion problems also arise in the refining of oils and in the manufacturing processes involved, but such corrosion is generally beyond the intended scope of this invention.

Hydrocarbon fluids are not usually corrosive to metals in the absence of an aqueous phase and of free oxygen except in the case of fluids containing corrosive materials such as hydrogen sulfide and the like. Also only in unusual circumstances are strongly acidic aqueous solutions encountered in handling refined products. Therefore, corrosion occurring in the transportation and storage of said refined products is dependent primarily on the presence of a practically neutral or an alkaline aqueous phase and free oxygen. In the presence of even a trace of aqueous material corrosion of the metal occurs according to the reactions generally accepted for the corrosion of metals in water and illustrated below.

The extent of the corrosion of metals in contact with an aqueous phase depends on the presence of oxygen gas in the case of neutral or alkaline solutions or on the evolution of hydrogen in the case of acid solutions. Thus, for metals in contact with a non-acidic aqueous phase the rate of corrosion is almost directly proportional to the concentration of free oxygen if other factors are constant.

The chemical reactions assumed to predominate during corrosion are the following as listed on page 14 of "Corrosion—Causes and Prevention," 2nd ed. (1935) by F. N. Speller:

(1) $Fe^{\circ} + 2H \leftrightarrows Fe + 2H^{\circ}$
metal ions ion atoms

(2) $2H^{\circ} + \frac{1}{2}O_2 \rightarrow H_2O$
atoms gas liquid

Assuming that in the presence of an aqueous phase, Reaction 1 is extremely rapid regardless of the pH of the aqueous medium, it follows that the rate and extent of corrosion associated with essentially neutral or with alkaline solutions depend on the occurrence and the rate of Reaction 2. Speller reports finding that in natural waters the rate of corrosion was almost directly proportional to the oxygen concentration up to about 6 cubic centimeters of oxygen per liter of water.

I have noted that the corrosion of metals in contact with refined hydrocarbon fluids and water or moderately alkaline solutions is dependent on the presence of free oxygen in the aqueous phase and/or the hydrocarbon fluid. In the case of a large quantity of a hydrocarbon liquid in contact with water and a metal surface, corrosion may be severe because oxygen gas is even more soluble in the hydrocarbon than in the aqueous phase and a plentiful supply of oxygen is assured at the metal surface by transfer from the hydrocarbon liquid. In order to restrict corrosion in such cases, the hydrocarbons might be substantially completely dehydrated and stored in the absence of water, but such operations are usually not economically feasible. Heretofore no feasible means of substantially reducing the oxygen content of hydrocarbon fluids has been available.

The removal of oxygen gas from water in order to control corrosion in piping systems has long been practiced through the use of so-called deactivators such as scrap iron. The de-aeration of water has also been practiced by heating and evacuation, followed in some cases by a chemical treatment with reagents such as a sulfite. Such methods, however, are not successfully adapted to the treatment of hydrocarbon fluids.

It is the principal object of this invention to restrict and/or prevent the internal corrosion of metal tanks, pressure vessels and pipelines used for storing or transporting refined hydrocarbon fluids.

Another object of this invention is to reduce the corrosion of metal container and pipelines for refined hydrocarbon fluids by substantially reducing the oxygen content of said fluids.

A further object is to prolong the service life and decrease the maintenance costs of metal equipment such as tanks, vessels, and pipelines used in storing and/or transporting refined hydrocarbon fluids by decreasing the internal corrosion thereof.

These and numerous other objects will be apparent from the following disclosure.

I have now discovered a process for reducing and/or deactivating the oxygen concentration of hydrocarbon fluids and hence reducing or limiting the oxygen content of any aqueous phase with

which said hydrocarbon fluids may be in contact. This process provides an efficient means of restricting the corrosion of corrodible metals in contact with said hydrocarbon fluids and the attendant aqueous phase.

Hydrocarbon oils, by reason of their ability to dissolve air and/or oxygen-containing gases, always contain an amount of free oxygen which may range from small concentrations of less than one up to 10 or more cubic centimeters per liter of oil. The concentration of dissolved oxygen depends on the processing or refining steps to which the hydrocarbons have been subjected. Other influencing factors are the precautions which may have been observed to limit the access of air to the hydrocarbon liquid subsequent to said processing steps.

I have now discovered that the oxygen concentration of hydrocarbon fluids which are stored or transported under appreciable super-atmospheric pressures may be reduced and controlled by addition to said fluids of a suitable reducing gas. Said reducing gas should be substantially non-reactive toward the hydrocarbons under the conditions employed but reactive with free oxygen therein. For example, I may employ hydrogen and/or carbon monoxide in quantities sufficient to react with free oxygen according to the following equations:

(3) $2H_2+O_2\rightarrow 2H_2O$

(4) $2CO+O_2\rightarrow 2CO_2$

Other reactions which may involve the reducing gases are the reduction of iron and other metal oxides which may be present as a result of previous corrosion, but reactions 3 and 4 predominate in most cases.

These reactions are relatively slow at atmospheric temperatures and pressures, but under the conditions employed in my process proceed faster than the corrosion Reactions 1 and 2 listed above. This is due to the remarkable accelerating effect of increased pressure on reactions of the reducing gases which compensates in part for the low temperatures employed. Further, and probably very important to the operation of the process, the metal oxides always present on corrodible metal surfaces are powerful catalysts for the reaction of hydrogen and carbon monoxide with oxygen and thus account for a great increase in reaction rates.

In accordance with my invention, hydrocarbon, which is usually in liquid or liquefied condition, which is generally of petroleum origin and which may be aliphatic such as paraffinic or olefinic, aromatic, naphthenic or of mixed type, and which contains oxygen dissolved therein, with or without a separate oxygen-containing gaseous phase, is commingled with a reducing gas, preferably hydrogen and/or carbon monoxide, in amount sufficient to react with all the oxygen present and preferably in great excess. The mixture is subjected at ordinarily encountered temperatures to elevated pressure sufficiently high to bring about combination of the reducing gas with a substantial portion of, and preferably at least 50% of, up to substantially all of, the oxygen present. The pressure may then be relieved after the treatment or may be continued so that further reaction occurs.

The invention may be applied to an existing body of hydrocarbon stored or moving in a corrodible container or conduit by introducing the reducing gas under pressure into intimate contact with the hydrocarbon, the mixture being subjected to reaction pressure for a period of time sufficient to react at least a substantial proportion of the oxygen therein. The pressure may then be released or preferably maintained throughout the period of storage or transportation.

For example as gasoline is pumped into a storage tank or pipeline it may be subjected in a separate zone to treatment in accordance with the present invention on its way to the storage tank or pipeline. Or it may be treated in accordance with the present invention in the storage tank or pipeline itself, as by introducing the reducing gas by means of suitable orifices or in other manner designed to effect intimate and prolonged intermixture with the entire body of gasoline. In the case of a pipeline, the gas may be introduced before, or at the point of, the introduction of the hydrocarbon to the pipeline and at suitable intervals thereafter as required.

The minimum pressure required will vary to some extent inversely with the temperature, but in general should be at least about 5 atmospheres absolute and preferably at least about 10 atmospheres. The temperature may be that normally obtaining under typical atmospheric conditions and will usually lie between about −30° F. and about 200° F. It will be understood that while the temperature of the air may not rise as high as this, the action of the sun's rays may raise the temperature within exposed storage tanks or pipelines somewhat above the temperature of the air. In general, however, no extraneous heat is deliberately applied to promote the reaction.

A separate gaseous phase in contact with the hydrocarbon liquid under treatment may or may not be present as desired. Frequently, as in pipelines or in the case of liquefied normally gaseous hydrocarbons which exhibit high solvent action on the reducing gas used, no such separate gaseous phase will be present. However it may be desired in some instances to employ such an excess of the reducing gas over theoretical required to combine with the free oxygen present that such a separate gaseous phase is present and maintained during storage.

Usually water will be present in the hydrocarbon liquid under treatment. This water may be dissolved in the hydrocarbon and may also be present in sufficient amount to form a separate aqueous phase in contact with or dispersed in the hydrocarbon.

While the invention is generally applied to hydrocarbons in liquid or liquefied form, it may be applied to gaseous hydrocarbons containing oxygen.

In accordance with my invention the dissolved oxygen content of the hydrocarbon liquid is reacted and thereby removed. I may use such an amount of hydrogen or CO and such reaction conditions as to reduce the oxygen content to less than about 0.2% by volume (2 cc. of oxygen per liter) and preferably to less than about 0.1% by volume (1 cc. of oxygen per liter). Where a gaseous phase is present, either by itself in the absence of any liquid hydrocarbon phase as where a compressed gaseous hydrocarbon is being treated in accordance with the present invention, or where an oxygen-containing gaseous phase is in contact with the hydrocarbon liquid, it is preferred to use such an amount of the reducing gas and such reaction conditions as to reduce the oxygen content of such gaseous phase to below about 0.002%, and better still to below about

0.001%, of oxygen by volume of said gaseous phase.

My process is economically applied as an additional step in the storage and transportation of hydrocarbon fluids since such operations may conveniently be carried out under substantial super-atmospheric pressures. Thus, in the storage of gasolines and/or liquefied petroleum gases in spheroid or other types of pressure tanks, the addition of hydrogen and/or carbon monoxide gas is an easily adaptable operation and pressures may be maintained within the containing vessels at such levels as to favorably influence the reaction between the reducing gas and the oxygen present in or above the hydrocarbon fluids.

Of even greater importance is the application of the process to the pipeline transportation of refined hydrocarbon fluids. Such pipeline transportation of gaseous or liquid hydrocarbons including natural gas, liquefied gases, gasoline, kerosene and the like is ordinarily carried out in a substantially closed system under high transmission pressures and at temperatures which are not high, seldom exceeding about 200° F. The hydrocarbon fluid with the associated aqueous phase and free oxygen is constantly under pressures ranging from maximum values of 1000 to about 1500 pounds gage at the discharge side of pumping stations to lower values ranging down to about 100 to 200 pounds gage at the intake side of subsequent pumping units. Under these conditions of high super-atmospheric pressures, the introduction of a suitable reducing gas at any point in the system initiates the reactions for the removal of oxygen or the conversion thereof to substantially inactive form. In addition to the high pressures, the presence of metal and metal oxides on the internal pipe surfaces promotes the oxygen-removing reactions and the restriction of corrosion.

The amount of reducing gas to be added in the process is determined by the oxygen content of the hydrocarbon fluid present or passing a metal surface to be protected. Ordinarily hydrogen and/or carbon monoxide is added in rather substantial excess of the amount theoretically required to react with oxygen according to Equations 3 and 4. The excess not only favors the reaction but is also a safety factor in case of later air contamination of the fluid. The upper limits for reducing gas addition may, of course, be partly determined by the solubility of said gases in hydrocarbon liquids, although this factor does not enter in the case of compressed petroleum hydrocarbon gases. However such an excess of the gas may be introduced as to form a separate phase thereof. Other considerations such as economic factors or the effect of the added gas on gas compositions may establish operating limits. The reducing gas may be added all at one point or additions may be made intermittently during a storage or transportation period to maintain a desired more or less constant concentration of active reducing material.

The following examples will provide specific data and illustrative conditions regarding the operation of the process, but neither the examples nor the foregoing theoretical considerations are to be construed as limiting the scope of the invention. Many additional applications will be evident in addition to those recorded herein.

Example 1

A blend of cracked and straight run gasoline was sampled and upon testing found to contain 4.11 cc. of oxygen per liter. This blend together with enough water to assure an aqueous phase undissolved in the gasoline was then placed in a steel container under a pressure of 10 atmospheres and at a temperature of 70° F. The container was liquid full so that no vapor space existed. After 72 hours the container was opened and the gasoline was found to contain 2.53 cc. of oxygen per liter. The reduction in free oxygen content was thus 38.5 per cent of the original oxygen content. This reduction was solely due to reaction of the oxygen gas during corrosion of the steel container according to Equation 2 of the above-listed corrosion reactions.

A second portion of the same type gasoline with an original free oxygen content of 4.98 cc. per liter was placed in a similar steel container with a similar proportion of water. Hydrogen gas amounting to 77.6 cc. per liter was added, and the pressure and temperature of the liquid full container were adjusted to 10 atmospheres and 70° F. respectively. The $2H_2:O_2$ ratio representing reacting gas volumes was 16:1. After 72 hours the container was opened and the oxygen content of the gasoline was found to be 1.06 cc. per liter. The reduction in the original content was thus 78.8 per cent, and in the presence of added hydrogen the increase in free oxygen removal was about 100 per cent over that found in the absence of hydrogen. Tests showed that this increased disappearance of oxygen was solely attributable to chemical reaction with the added hydrogen. Moreover at the end of the 72 hour period most of the hydrogen still remained in unreacted form and was available for future protection. Furthermore the corrosion of the vessel at the end of this run was less than the corrosion in the comparative run described in the preceding paragraph.

A third portion of the same type gasoline was stored under identical conditions without added hydrogen and in a glass-lined steel container. After 72 hours, there was substantially no decrease in oxygen content, thus showing that oxygen was not consumed by reaction with the gasoline.

Example 2

Two samples of a straight run gasoline were chosen and the free oxygen content of each determined. One sample was placed in a steel container with water but without added hydrogen; the second was placed in an identical container under identical conditions except that sufficient hydrogen gas was added to produce a $2H_2:O_2$ ratio of 16.5:1. The containers were liquid full and the pressures were 200 pounds per square inch gage at 77° F. for the first and at 80° F. for the second. Room temperatures were used, which varied from 60° F. to 80° F. during 24 hours, the temperature averaging close to 70° F. After 72 hours storage the containers were opened and the oxygen content of each gasoline sample was determined with results tabulated below.

Sample No.	Added H_2	Residual O_2 in gasoline	Added O_2 content	Initial total O_2 content	Final O_2 content	Per cent reduction O_2 content
1	0	0.26	4.60	4.86	3.23	33.9
2	79	0.67	4.11	4.78	1.68	64.8

All figures except per cent in cc./liter.

Again the extent of free oxygen removal was almost 100 per cent greater in the case of the

sample containing added hydrogen than in the case of sample 1 where oxygen removal was associated only with corrosion of the container. Moreover this removal of oxygen was attributable chiefly to reaction with the hydrogen and corrosion of the vessel was materially less even in short time of the test.

Example 3

The gasoline of Example 2 was used in comparative tests under conditions identical with Example 2 except that carbon monoxide was used instead of hydrogen. With a $2CO:O_2$ ratio of 14:1 the reduction in free oxygen content was 58 per cent compared to 32 per cent in the container to which no reducing gas was added. As before this reduction in free oxygen content was attributable to reaction with the carbon monoxide and was accompanied by reduced corrosion.

These examples indicate the extent to which corrosion of the corrodible metal containers was restricted when hydrogen and carbon monoxide were added to reduce the oxygen content of the hydrocarbon liquid.

Reducing gases especially suitable for the process are hydrogen and carbon monoxide or mixtures thereof with each other or with other inert nonoxidizing gases and preferably substantially free of oxygen and of any components not substantially inert toward the hydrocarbon fluids and/or the metal surfaces. It will be obvious that it is highly desirable to avoid the introduction of oxygen or gases containing it or other oxidizing impurities when the purpose of the process is to reduce corrosion and the free oxygen content of the materials present.

The reducing gases which are useful are substantially pure hydrogen, substantially pure carbon monoxide, substantially pure mixtures of hydrogen with carbon monoxide, and similar gases free from hydrogen sulfide. The gas used should be free from oxygen, hydrogen sulfide or other reactive or harmful constituents. Use of a gas selected from the group consisting of substantially pure carbon monoxide and hydrogen is highly preferred. Since the components of such gases or mixtures are substantially non-condensible under ordinary conditions they are easily separable from hydrocarbon liquids of the nature of gasoline when their function is completed. It is usually desirable for economic reasons to use gases with relatively large concentrations of the active reducing components since the volume required is calculated on the basis of the active components. When flue gases or combustion gases are available free of oxygen they may be utilized for the carbon monoxide content, and water and carbon dioxide may be removed prior to use.

I am aware that it has been proposed (U. S. 2,029,748) to generate nascent hydrogen by the action of an added electrolyte and metal in the bottom of a body of gasoline stored in an iron storage tank, for the purpose of preventing gum and color-formation in the gasoline. Such a process has not attained any commercial usefulness, so far as I am aware, apparently because the complications and expense incident thereto render it impracticable. The present invention is markedly different from such a process because I add previously formed gaseous hydrogen as such directly to the hydrocarbon instead of going through the complications incident to generation of nascent hydrogen in situ. In my process no electrolyte is needed which itself would cause corrosion of the iron and other undesirable side reactions. Moreover it has not been proposed, so far as I am aware, to maintain a mixture of gasoline and molecular hydrogen under sufficient pressure to cause chemical reaction between the hydrogen and dissolved oxygen. At most previously proposed process involves merely flushing of the gasoline with molecular hydrogen formed from the nascent hydrogen, at substantially atmospheric pressure, and wholly fails to teach the bringing about of a chemical reaction between the hydrogen and any dissolved oxygen. Atmospheric pressure is insufficent to bring about this reaction. Moreover there is no teaching of any direct analogy between the mechanism of gum-formation and the mechanism of corrosion of the container. In addition my process is readily adapted to transportation of hydrocarbons as in a pipeline. In pipeline transportation the generation of nascent hydrogen would be wholly impracticable and the maintenance above the hydrocarbon liquid of a hydrogen atmosphere resulting therefrom would likewise be impossible. Even in the case of pipeline transportation of gaseous or vapor hydrocarbons, maintenance of a separate phase of hydrogen would be impossible. Moreover the pressures used in pipeline transportation would necessarily far exceed anything contemplated in the prior process under discussion. Another point of distinction is that in my process the reducing gas may be introduced to or commingled with the hydrocarbon either in a separate treating zone as the hydrocarbons is fed into the storage tank or pipeline or may be pumped into the hydrocarbon in the storage tank after the hydrocarbon has been introduced into the storage tank or may be pumped into the storage tank or pipeline simultaneously with the hydrocarbon either separately therefrom or with the hydrocarbon.

The corrodible metals contemplated by the present invention usually comprise either iron or copper.

The present invention is applicable whether or not water or other aqueous material be present in contact with the hydrocarbon and whether or not such aqueous material be in solution in the hydrocarbon or present as a separate aqueous phase.

I claim:

1. The process for reducing the corrosiveness of hydrocarbon fluids containing oxygen upon metals which comprises commingling with a reducing gas in sufficient quantity to react with a substantial portion of said oxygen and subjecting the mixture to a pressure of at least about 5 atmospheres at a temperature of from about −30° to about 200° F. to effect said reaction.

2. A process for the restriction of the corrosion of corrodible metals in contact with hydrocarbon fluids associated with free oxygen and an aqueous phase which comprises adding to said hydrocarbon fluids in a closed system under at least about 5 atmospheres pressure and at ordinary temperatures carbon monoxide gas substantially in excess of theoretical quantities required for reaction with the free oxygen present in said system.

3. A process for the restriction of the corrosion at ordinary temperatures of corrodible metals in contact with refined hydrocarbon fluids associated with free oxygen and an aqueous medium which comprises adding to said hydrocarbon fluids in a closed system under at least about 5 atmospheres pressure an effective amount of hydrogen gas in molecular form whereby the oxygen content of said system is substantially reduced.

4. A process for the restriction of the corrosion at ordinary temperatures of corrodible metals in contact with refined hydrocarbon fluids associated with free oxygen and an aqueous medium which comprises adding to said hydrocarbon fluids in a closed system under at least about 5 atmospheres pressure an effective amount of carbon monoxide whereby the oxygen content of said system is substantially reduced.

5. The method of preventing corrosion of corrodible metal containers used for the storage of hydrocarbon fluids containing oxygen which comprises introducing into said fluids stored in said container an excess over theoretical required to combine with said oxygen of a reducing gas selected from the group consisting of hydrogen and carbon monoxide and storing the resulting mixture in said container at atmospheric temperatures and under a pressure of at least about 5 atmospheres.

6. The method of preventing corrosion of corrodible pipelines used for the transportation of hydrocarbon fluids containing oxygen which comprises introducing into said fluid in said pipeline an excess over theoretical required to combine with said oxygen of a reducing gas selected from the group consisting of hydrogen and carbon monoxide and transporting the resulting mixture in said pipeline at atmospheric temperature and under a pressure of at least about 5 atmospheres.

7. The method of preventing corrosion of corrodible pipelines used for the transportation of hydrocarbon liquid containing oxygen which comprises introducing into said liquid at the point where it enters said pipeline an excess over theoretical required to combine with said oxygen of a reducing gas selected from the group consisting of hydrogen and carbon monoxide, transporting the resulting mixture in said pipeline at atmospheric temperature and under a pressure of at least about 5 atmospheres, and at intervals in said pipeline introducing additional portions of said gas.

8. The process for reducing the corrosiveness of hydrocarbon liquids containing oxygen upon metals which comprises commingling said liquids with molecular hydrogen in excess of the amount theoretically needed to react with the oxygen in the hydrocarbon liquids at a pressure of substantially 200 pounds per square inch gage and a temperature of between 60 and 80° F.

9. The process for reducing the corrosiveness of hydrocarbon liquids containing oxygen upon metals which comprises commingling said liquids with molecular hydrogen in excess of the amount theoretically needed to react with the oxygen in the hydrocarbon liquid at a pressure of at least 5 atmospheres absolute and a temperature of between —30° F. and 200° F.

10. The process for reducing the corrosiveness of hydrocarbon liquids containing oxygen upon metals which comprises commingling said liquids with a reducing gas of molecular form selected from the group consisting of hydrogen and carbon monoxide in excess of the amount theoretically needed to react with the oxygen in the hydrocarbon liquid at a pressure of at least 5 atmospheres absolute and a temperature of between —30° F. and 200° F.

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