

**LOW ENERGY SURFACES FOR
REDUCED CORROSION AND FOULING**

FIELD OF THE INVENTION

[0001] This invention relates to a method for reducing fouling and corrosion of metal surfaces. More particularly, metal surfaces such as piping and heat exchangers that transport or contain corrosive and contaminated materials can be protected by formation of organometallic coatings that are in the range of monolayers in thickness.

BACKGROUND OF THE INVENTION

[0002] Fouling of metal surfaces such as the piping, heat exchangers and reactors used in refineries and chemical plants result in significant costs including cleaning and equipment down times. Such fouling can occur from a number of sources such as crudes, distillates, process feedstocks and the like. In many instances, costs may also include energy costs associated with more extreme operating conditions necessitated by the presence of foulants such as coke and attendant safety issues. For petroleum refiners, the costs associated with cleaning and equipment down times can run into annual costs in the hundreds of millions of dollar range.

[0003] There have been a number of approaches to mitigating fouling, including coatings for metal surfaces. One approach for forming a protective surface film is by depositing a layer of silica resulting from oxidative decomposition of an alkoxy silane in the vapor phase on the metal surface. Another approach is to passivate a

-2-

reactor surface subject to coking by coating the reactor surface with a layer that is from several microns to several millimeters thick of a ceramic material deposited by thermal decomposition of a silicon containing precursor in the vapor phase. Both approaches result in a surface oxide with relatively high surface energy that can attract unwanted deposits of the surface. While these coatings can have some value in preventing corrosion, they have proved to be ineffective in reducing fouling.

[0004] Other coatings are directed to polymeric materials such as polyethylene and polyvinylfluoride with low surface energy used in biofouling for aqueous environment at ambient conditions. The polymeric coating cannot withstand higher temperature conditions typical of refinery operations and are not effective in hydrocarbon fouling.

[0005] Physical cleaning by hydroblasting or steam injection has been used to clean fouled equipment. Chemical mitigation can also be employed. This typically involves the use of anti-foulants to remove or minimize creation of unwanted deposits. Examples of such anti-foulants include sulfur- and phosphorus-containing compounds and phenolic compounds.

[0006] The typical coatings for industrial conduits are generally in the micron to millimeter range in thickness. This is usually to ensure good surface coverage as well as provide a protective layer of sufficient thickness to be robust during operating conditions. However, such thick coatings may limit heat exchange.

[0007] It would be desirable to have an effective and inexpensive coating to mitigate both corrosion and fouling in refinery and chemical process equipment

including piping and heat exchangers in which the coating is in the range of monolayers thick and has low (optimum) surface energies.

SUMMARY OF THE INVENTION

[0008] This invention relates to a process for mitigating both corrosion and fouling of metal surfaces which comprises: contacting the metal surface with an organometallic compound capable of bonding to the metallic surface and forming a layer of organometallic molecules which is 1 to 10 molecular layers thick, which layer will not undergo substantial decomposition at temperatures up to 450°C and which layer has a surface energy lower than 50 millijoule/m².

[0009] Another embodiment relates to a process for mitigating fouling and corrosion in refinery and chemical plant equipment having metal surfaces which comprises: contacting the metal surface with an organometallic compound capable of bonding to the metallic surface and forming a layer of organometallic molecules which is 1 to 10 molecular layers thick, which layer will not undergo substantial decomposition at temperatures up to 450°C, which layer has a surface energy lower than 50 millijoule/m², and which layer is deposited on greater than 25% up to 100% of the metal surface.

[0010] Yet another embodiment relates to a process for mitigating fouling in refinery and chemical plant equipment having metal surfaces which comprises: heating the metal surface in an oxygen-containing atmosphere at temperatures of from 100°C to 500°C for a time sufficient to clean said metal surface of carbonaceous residues, contacting the metal surface with an organometallic compound capable of bonding to the metallic surface and forming a layer of

-4-

organometallic molecules which is 1 to 10 molecular layers thick, which layer will not undergo substantial decomposition at temperatures up to 450°C, which layer has a surface energy lower than 50 millijoule/m², and which layer is deposited on greater than 25% up to 100% of the metal surface.

[0011] A still further embodiment relates to a process for mitigating fouling in refinery and chemical plant equipment having metal surfaces containing corrosion layers which comprises: contacting a metal surface containing a corrosion layer with at least one of high pressure water or steam to produce a water or steam cleaned metal surface; heating the water or steam cleaned metal surface in an oxygen-containing atmosphere at temperatures of from 100°C to 500°C for a time sufficient to further clean said metal surface of carbonaceous residues, contacting the further cleaned metal surface with an organometallic compound capable of bonding to the metallic surface and forming a layer of organometallic molecules which is 1 to 10 molecular layers thick, which layer will not undergo substantial decomposition at temperatures up to 450°C, which layer forms a surface having a water contact angle between 95 to 160 degrees, and which layer is deposited on greater than 25% up to 100% of the metal surface.

[0012] Another embodiment relates to a metal surface capable of resisting fouling when exposed to corrosive or coke forming at atmospheric or greater pressures which comprises a metal surface and a layer of organometallic molecules deposited on said metal surface, said layer of organometallic molecules being 1 to 10 molecular layers thick, which layer will not undergo substantial decomposition at temperatures up to 450°C, which layer has a surface energy lower than 50 millijoule/m², and which layer is deposited on greater than 25% up to 100% of the metal surface.

-5-

[0013] Treatments with silicate sols, or paints rich in silicon or aluminum typically produce relatively thick surfaces (micron to millimeter) that can provide a physical boundary that protects the underlying metal from corrosion. However, such treatments will not have low surface energies if the surface terminates in an oxide/hydroxide surface layer. Uses of silanes for "chemical vapor deposition" are also known but with the intent to diffuse Si, C, H and other elements into the metal surface using high temperatures (e.g. 600°C); the result is that the surface, though non-metallic, can still have a high surface energy and will not reject potential foulants.

[0014] In the present invention, the surface is created by reaction of an organometallic such that the organic moiety is retained (chemisorbed), yielding a stable, thin near monolayer surface that is more resistant to spalling and cracking than thicker coatings and has a low surface energy needed to discourage and reject potential deposits. Thus, the prior art uses physical barriers to coat metals but the present invention uses a chemical modification approach to protect metal surfaces.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Figure 1 is a photograph showing the scanning electron microscopy micrographs of steel coupons exposed to hot crude together with corresponding graphs showing the sulfur content using energy dispersive spectroscopy.

[0016] Figure 2 is a photograph showing a cross section of the scanning electron microscopy micrographs of steel coupons exposed to hot crude.

-6-

[0017] Figure 3 is a graph showing wt.% silicon as a function of wt.% carbon on various steel samples.

[0018] Figures 4A and 4B are plots of Gibbs Free Energy vs. surface energy (4A) and the corresponding plot of surface energy vs. water contact angle (4B).

[0019] Figure 5 is a graph showing surface energy as a function of water contact angle.

[0020] Figure 6 is a photograph showing the fouling of carbon steel coupons as a function of water contact angle.

DETAILED DESCRIPTION OF THE INVENTION

[0021] In typical refinery and chemical plant processes, many feedstocks are prone to produce fouling of process equipment. Such feeds include crude which can contain contaminants that foul equipment by depositing residue and/or corrosive components. Examples of such contaminants include salts, metals, sulfur- and nitrogen-containing species, distillation bottoms and the like. Corrosive components include acidic compounds such as sulfur-containing acidic species and naphthenic acids. Such contaminated feeds produce coke and other undesirable deposits that limit flow and heat exchange.

[0022] This invention relates to a metal surface and a process using said metal surfaces wherein an organometallic coating is used to protect metal surfaces, especially those present in refinery and chemical plants. Most refinery and chemical plant process equipment is made from carbon steel and alloys thereof.

-7-

Stainless steel is more resistant to corrosion but is less frequently employed as a metal of fabrication because of the increased cost.

[0023] The organometallics used in the present process are those which are capable of bonding to a metal surface and which will not decompose at the temperature to which the metallic surface is exposed. Most organometallics used in the prior art to protect metallic surfaces are employed as precursors and are converted to oxides which function as the protective coating. In the present case, the organometallic compound, not its oxide, functions as the protective coating. Thus, the present organometallic coating functions as a chemical protective layer in the monolayer range as compared to a physical barrier provided by the much thicker prior art coatings.

[0024] In the organometallic compounds used as coating materials, the metallo components of the organometallic compounds are from Groups 4 to 15 based on the IUPAC format for the Periodic Table having Groups 1 to 18, preferably Group 14, more preferably silicon and tin, especially silicon. The organo components of the organometallic compounds are hydrocarbyl groups having from 1 to 30 carbon atoms, preferably from 1 to 20 carbon atoms, more preferably 1 to 10 carbon atoms. The hydrocarbyl groups may be aliphatic or aromatic groups which aliphatic or aromatic groups may be substituted with functional groups such as oxygen, halogen, hydroxy and the like. Preferred hydrocarbyl groups include methyl, ethyl, methoxy, ethoxy and phenyl. Preferred organometallic compounds include alkylsilanes, alkoxy silanes, silanes, silazanes and alkyl and phenyl siloxanes. Especially preferred compounds include alkyl- or alkoxy silanes having from 1 to 20 alkyl or alkoxy groups, especially tetraalkoxy compounds such as

tetraethoxy-silane, alkylsilanes having from 1 to 6 alkyl groups, especially hexamethyl-disiloxane.

[0025] The organometallic coating on the metallic surface should have a low energy surface. By low energy surface is meant a coating having a surface free energy lower than 50 milliJoules/square meter (mJ/m^2), preferably between 21 to 45 mJ/m^2 . The surface free energy is determined by measuring the water contact angle. The low surface energy of the layer ensures a low interfacial energy at, for example, the interface between crude oil and the coated layers, even at the higher temperature conditions found in typical heat exchangers, e.g., 200°C to 400°C for a crude pre-heat exchanger train. This in turn provides for a weak interaction of foulants and corrosive species with the surface resulting in a reduction in fouling and corrosion rate.

[0026] The amount of covering of the organometallic coating layer ranges from greater than 25% of the metal surface to 100% of the metal surface, preferably from 50 to 100%, more preferably from 80 to 100%. The amount of metal surface covered is most preferably 100% or as close to 100% as possible.

[0027] The metal surface to be protected is preferably clean of carbonaceous deposits such as coke. This is important in continuous processes in which a feed is heated while in contact with a metal surface such as pipes used in refinery and chemical plant service, heat exchangers and furnace tubes. After standard initial cleaning with a light cycle oil, other light oil or other solvent and high pressure water jetting or high pressure steam cleaning, the metal surface is preferably cleaned by heating in the presence of an oxygen-containing gas, preferably air, at temperatures of from 200°C to 500°C, preferably 300°C to 400°C for a time

-9-

sufficient to remove the desired deposits, particularly carbonaceous deposits. The heating typically occurs at atmospheric pressure although higher pressures are acceptable. If salts are present, a water wash may be used to remove salts. The cleaned metal surface may also be treated with a solution of metal salt to enhance the effectiveness of the organometallic coating process. For example, a carbon steel surface may be first treated with a Cr salt solution.

[0028] The cleaned and heated metal surface is then subjected to organometallic coating by exposing the heated metal to organometallic compound in the gaseous phase, liquid phase or mixed liquid-vapor phase. The organometallic compound may be sparged into the vapor state using a carrier gas such as nitrogen or the organometallic may be mixed with a carrier liquid such as cyclohexane, xylene, water carbon tetrachloride, chloroform, fuel oil, lube boiling range hydrocarbon, crude oil and the like as a dilute solution, e.g., up to 5 vol.%. The organometallic coating process should preferably take place in the absence of an oxygen-containing gas. The temperature of the coating process may range from ambient to 500°C. The upper temperature range for coating is a function of the stability of the particular organometallic used for coating.

[0029] The extent of the surface modification by organometallic coating can be measured using water contact angles. This test measures the contact angle of water in contact with the modified metal surface. An example of a test procedure for measuring water contact angles is ASTM D-5725. High water contact angles imply high hydrophobicity and good coverage of the underlying metal (or metal oxide/sulfide) surface by the organometallic coating. For the metal surfaces modified according to the invention, measured water contact angles are between 95 to 160 degrees, preferably 110 to 150 degrees.

-10-

[0030] The thickness of the organometallic coating ranges from 1 to 10 molecular layers thick, preferably 1 to 3 molecular layers thick, more preferably a monolayer thick. The thickness of the molecular layer may be controlled by the deposition process, e.g., by controlling the time of exposure of the metal surface to the organometallic compound and controlling the pressure under which the coating is applied.

[0031] Operating temperatures for the metal surfaces coated with organometallic molecules according to the invention should be maintained below 450°C, preferably below 400°C, more preferably below 350°C. Some decomposition of organometallic coating may occur depending on the nature of the organometallic employed as coating and the operating temperature employed. For example, phenyl silanes as coating agent can be stable at higher temperatures and may be used in more severe service than alkyl silanes. By "substantial decomposition" of the layer of organometallic molecules is meant that the organometallic molecules in the coating (covering) layer are reduced to less than 25% coverage of the metal surface.

[0032] The behavior of the present organometallic coatings is believed to be at least in part a function of the organo moiety. While not wishing to be bound to any particular theory, it appears that the organo moiety minimizes the interaction energy with both polar and non-polar hydrocarbons and mitigates fouling and corrosion in this manner. Minimizing corrosion can be linked with minimizing fouling. For example, corrosion tends to increase the metal surface area creating a trap for foulants. Ordinary ceramic coatings of metals surfaces rely on a physical barrier to mitigate corrosion. However, ceramic coatings will not be as effective as

-11-

organometallics because surface energies may still be high, i.e., greater than 100 mJ/m². The same reasoning applies to oxide coatings used to provide a physical barrier. Thus, metals, particularly steels and alloys thereof, can be provided with a low surface energy monolayer or near monolayer of organometallic coating that resists both corrosion and fouling deposits in refineries and chemical plants. Examples of such uses include crude preheat trains, steam cracker transfer lines, and transfer lines used in polymer manufacture. The material to be protected by organometallic coating may also be other metals as well as non-metal materials such as ceramics.

[0033] An example of a refinery process which illustrates the invention are heat exchangers common to many refinery units such as boilers. These exchangers are periodically taken out of service for cleaning resulting in unit down time as well as cleaning costs. In the present process, the heat exchangers after traditional cleaning would be heated in air to remove carbonaceous deposits and then coated with an organometallic such as hexamethyl disiloxane (HMDSO) by exposing the heated (300°C to 400°C) clean metal surface to HMDSO at low pressure in an oxygen-free environment until a coating is achieved, typically in less than 1 hour. The unit is then ready to be returned to service.

[0034] The invention is further illustrated in the following examples.

EXAMPLE 1

[0035] This example illustrates that very thin (near monolayer) coatings of an organosilane show much reduced formation of iron sulfide scale.

-12-

[0036] Three 304 stainless steel coupons and three carbon steel coupons were treated in a stainless steel tubular reactor with hexamethyl disiloxane (HMDSO) at 20 torr and temperatures of 300°C, 400°C and 500°C for 30 minutes. After treatment, the reactor was evacuated to 1×10^{-6} torr and cooled to room temperature and the coupon was discharged in air for further testing. A comparative treatment was performed with three 304 stainless steel coupons and three carbon steel coupons with same thermal history but without exposure to HMDSO. The surface coverage of Si was measured using x-ray photoelectron spectroscopy (XPS) with results presented in the following Table 1.

TABLE 1
% Silicon at Surface (by XPS) at Temperature

Temperature, °C	Carbon Steel (A36)	Stainless Steel (A304)
300	5.6	6.56
400	1.3	5.8
500	not measured	2.0

[0037] In Table 1, surface Si content measured by XPS was 6.56 % at 300°C treatment. For a relatively smooth surface, this is estimated to be close to a complete monolayer. The stainless steel coupon showed that there is about 25% coverage even at 500°C. The surface species initially generated are believed to comprise tri-methyl silyl links through a surface oxygen to a metal site.

[0038] The coupons treated at 300°C were tested in a mini-bomb with Topacio crude at 350°C for 24 hours. The resulting coupons were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

-13-

[0039] SEM micrographs shown in Figure 1 were obtained from the exterior surface of the coupons. The micrographs demonstrate that with Topacio crude exposure HMDSO treated coupon resulted in a surface that shows very little variation while thermally treated coupon shows a surface with rough texture. In addition EDX (Energy Dispersive X-ray Spectroscopy) analysis of representative surface from the coupons show that HMDSO treated coupon has minimal presence of sulfur while thermally treated coupon has a higher amount of sulfur present on the coupon.

[0040] SEM micrographs shown in Figure 2 were also obtained from cross sections of the same coupons. The images from HMDSO treated coupon shows very little variation along the edge of the coupon/epoxy interface while thermally treated coupon shows very rough texture along the edge of the coupon/epoxy interface. The coupon/epoxy interface shows the roughness of the exterior surface of the coupons. The results from the external surface analysis and cross sectional analysis suggest that thermally treated coupons suffered corrosion damage when exposed to Topacio crude while HMDSO treated coupons showed minimal corrosion damage.

[0041] All micrographs from HMDSO treated coupon shows no transition region from the coupon to epoxy suggesting that the layer deposited from HMDSO is too thin to be observed with SEM magnification.

EXAMPLE 2

[0042] This example is directed to a procedure to provide coverage of a steel surface and illustrates the importance of providing a surface from which most of

-14-

the carbonaceous deposits have been removed. Carbon steels tend to retain more carbonaceous contaminants than stainless steels and for best effect should be pretreated. A preheat in air or O₂ at about 350°C may be adequate to eliminate any carbonaceous residue in many cases. This methodology can also apply to treatment of exchangers previously in service. Various samples of steel bearing different amounts of carbon deposits were treated with HMDSO at 20 torr pressure and 300°C for varying time periods to remove different amounts of carbon deposits from the steel samples. The results are shown in Figure 3 which is a graph showing wt.% silicon versus wt.% carbon based on the weight of the coupon. In Figure 3, T1A is a carbon - 1/2 % molybdenum steel, 1018 is a carbon steel, and 310 and 304 are stainless steels. Run 5 is also a stainless steel. As can be seen from Figure 3, the wt.% Si on the steel samples is dependent on the amount of carbonaceous deposit remaining. At about 30 wt.% carbon, the amount of Si starts to increase and continues to increase as the amount of carbon remaining decreases.

[0043] If higher temperatures are needed to burn off a residue, it may be necessary to follow this step with a water wash and dry to remove salts that can migrate from the bulk to the surface. For example, sodium and chlorine populations grow on carbon steels at temperatures above 350°C and should be avoided or removed before attempting treatment to obtain maximum HMDSO coverage.

[0044] Modification can be affected over a range of conditions and from different media. Vacuum deposition of HMDSO is effective in providing surfaces that resist corrosion and fouling as illustrated by experiments in Example 1 above.

-15-

[0045] Surfaces can be modified from a mixed liquid-vapor phase using, e.g., high boiling lube hydrocarbons to solubilize the organosilane. Treatments can also be performed by sparging an inert gas (e.g. N₂ or Ar) into liquid modifier to transport vapor to the reaction site. In this mode treatment times may need to be several hours to ensure a near monolayer is formed. Treatment temperatures may range from 200°C to 500°C for stainless steel, and are preferably 300°C to 400°C for carbon steel.

[0046] Reagent choice may vary depending on the intended service and/or limits of conditions for treatment. Various alkoxysilanes and alkyl and aryl substituted siloxanes and silazanes are examples of organometallics.

EXAMPLE 3

[0047] This example demonstrates that in order to obtain low adsorption energy, the water contact angle should be greater than about 98 degrees. Figures 4A and 4B are plots of Gibbs Free Energy versus surface energy (4A) and the corresponding plot of surface energy versus water contact angle (4B). The strength of adsorption of the foulant materials from a liquid onto the surface can be determined using the Gibbs and adsorption isotherm equations. The Gibbs equation relates the interfacial coverage to the interfacial energy and the adsorption isotherm equation, such as the Langmuir adsorption isotherm equation relates the interfacial coverage to the Gibbs free energy of adsorption. Combining these two equations one obtains the relationship between the minimum Gibbs free energy of adsorption and the interfacial energy. The interfacial energy is a function of the surface energy of the liquid and the surface energy of the solid. Since the surface energy of the solid is low, the interaction between the solid and the oil is a weak

-16-

dispersion. Thus, the interfacial energy, γ_{LS} , can be written as a function of the surface energy of the solid, γ_s , and the surface energy of the liquid, γ_L as:

$$\gamma_{LS} = (\sqrt{\gamma_s} - \sqrt{\gamma_L})^2$$

[0048] Curve A of Figure 4A shows the variation of interfacial energy as a function of solid surface energy, using a surface energy of the liquid, $\gamma_L = 32.65$ mJ/m². Curve B of Figure 4A shows the variation of minimum Gibbs free energy of adsorption with the solid surface energy. It shows that the adsorption is weak if the interfacial energy is low and the surface energy of the solid is close to the surface energy of the liquid.

[0049] The surface free energy of the solid is determined using a water contact angle measurement device. Figure 4B shows the relationship between the surface energy of the solid and the water contact angle, θ , for low surface energy solids using:

$$\gamma_s = 66.613(1 + \cos\theta)^2$$

To obtain a surface energy lower than 50 mJ/m², a water contact angle should be larger than 98 degrees.

EXAMPLE 4

[0050] A measure of the extent of surface modification by the surface modification step can be made using a device to calculate the extent to which water beads up on the treated surface (the water contact angle). High angles imply high

hydrophobicity and good coverage of the underlying substrate by the modifier.

There is a correlation between reduced fouling propensity and higher water contact angle, as can be seen from Figure 5 which is a graph showing surface energy as a function of water contact angle.

[0051] The water contact angles were measured using a Kruss Automated Angle tester with a DSA 100 Device Control Panel. The instrument was calibrated using high purity water. The calculations of water contact angles were made using images captured on video camera. The contour of the drop is traced and the curve tracing used to calculate the average contact angle. When the surface is uneven, the drop contour cannot be seen all the way down to the surface and a certain distance is excluded from the water contact angle analysis. The corresponding contour is compiled from the drop contour that can be measured. Data from captured images are averaged in the water contact angle calculations. The left and right contact angles from several measurements are averaged to give an overall contact angle in degrees.

[0052] Carbon steel coupons were exposed to Maya whole crude at 350°C for 3 hours to simulate conditions that might exist in a crude pre-heat exchanger. The coupons were variously modified with octatridecyl trichloro silane to affect different levels of coverage. Multiple treatments with an intervening air calcination step generated coupons with the highest contact angles (above 130 degrees). These coupons formed very little measurable deposit whereas the coupons with lower contact angles and particularly the untreated carbon steel coupon showed significant deposits, measurable by both a weight gain and by a decline in electrical resistivity. Figure 6 shows the fouling of the coupons as a function of water

-18-

contact angle. The high water contact angles are achievable on steel surfaces that are fresh or have previously been in surface and subsequently cleaned.

[0053] Rendering a high water contact on a metal surface is achievable on steel surfaces that are either fresh or those that have been in service. The instant procedure for modifying metal surfaces has been found to be effective even on heat exchanger tubes that have been in service and developed a corrosion layer. As long as these tubes are cleaned by conventional means, the residual adhered corrosion layer provides an excellent substrate for subsequent surface modification, following the same steps as with fresh metal tubes, that is an air heating step followed by treatment with, for example, an organosilane.

[0054] Heat exchanger tubes from prior service are usually found to have a combination of iron sulfides mixed with carbonaceous deposits. Refiners clean such tube bundles with high pressure water ("hydroblasting") to scour loosely held residues from the tube surface, both inside and out, then return them to service. Tubes undergoing this treatment usually retain a sulfide/oxide layer that is different from the original fresh metal surface that typically comprises iron and iron oxides (if carbon steel) or perhaps spinel type oxides of Fe and Cr if higher alloy steels are used.

[0055] Carbon steel and 5-Cr steel tubes that have been in service for months or years in crude preheat service typically show low to moderate water contact angles (80 degrees or less) following hydroblasting and drying. This is correlated with a high surface energy, associated with mixed metal oxides and or sulfide eg FeS. For example, SEM shows that the carbon steel tubes retained a 20 micron thick iron sulfide layer after hydroblasting and drying.

-19-

[0056] Subsequent air heating at 350°C for 1 hr. further lowers the water contact angle (i.e. raises the surface energy) indicating that a very hydrophilic (presumably hydroxylated) surface is generated. This can be a good substrate for subsequent reaction with the right surface modifier. Following treatment with e.g., a silane such as hexamethyldisiloxane, very high water contact angles are subsequently achieved illustrating near complete coverage of the surface by the modifier. These are believed to be surfaces that will effectively resist further corrosion and mitigate fouling by deterring deposit formation, including carbonaceous residues, inorganic salts etc.

[0057] Table 2 below indicates that effective surfaces to resist fouling (and corrosion) can be generated whether the surface is fresh or has been in service.

TABLE 2

		<u>Water Contact Angle, Degrees</u>	
		<u>Carbon Steel</u>	<u>5-Cr Steel</u>
Fresh Metal Tubing	As Received	60 to 80	80 to 90
	Air Heated, 350°C, 1 hr.	-	about zero
	Treated with Silane Vapor (HMDSO), 350°C, 1 hr.	105 to 110	110 to 115
Tubes from Prior Service (Crude Preheat)	As Received	50 to 90	40 to 90
	Air Heated, 350°C, 1 hr.	about zero	about zero
	Treated with Silane Vapor (HMDSO), 350°C, 1 hr.	115 to 130	120 to 140

Note: Range of values indicates typical surface in homogeneities from sample to sample and across the surface of a given sample

CLAIMS:

1. A process for mitigating fouling of metal surfaces which comprises: contacting the metal surface with an organometallic compound capable of bonding to the metallic surface and forming a layer of organometallic molecules which is 1 to 10 molecular layers thick, which layer will not undergo substantial decomposition at temperatures up to 450°C and which layer has a surface energy lower than 50 millijoule/m².

2. A process for mitigating fouling in refinery and chemical plant equipment having metal surfaces containing corrosion layers which comprises: contacting a metal surface containing a corrosion layer with at least one of high pressure water or steam to produce a water or steam cleaned metal surface; heating the water or steam cleaned metal surface in an oxygen-containing atmosphere at temperatures of from 100°C to 500°C for a time sufficient to further clean said metal surface of carbonaceous residues, contacting the further cleaned metal surface with an organometallic compound capable of bonding to the metallic surface and forming a layer of organometallic molecules which is 1 to 10 molecular layers thick, which layer will not undergo substantial decomposition at temperatures up to 450°C, which layer forms a surface having a water contact angle between 95 to 160 degrees, and which layer is deposited on greater than 25% up to 100% of the metal surface.

3. The process of claims 1 or 2 wherein the metal in the organometallic compound is from Groups 4 to 15.

-21-

4. The process of any preceding claim wherein the layer of organometallic molecules is deposited on 80 to 100 % of the metal surface.
5. The process of any preceding claim wherein the metal surface is heated at temperatures from 100°C to 500°C in an oxygen-containing atmosphere prior to contacting with organometallic compound, and is carbon steel or stainless steel.
6. The process of any preceding claim wherein the metal in the organometallic compound is silicon.
7. The process of any preceding claim wherein the organo moiety in the organometallic compound is a hydrocarbyl group from 1 to 30 carbon atoms.
8. The process of any preceding claim wherein the hydrocarbyl group is aliphatic or aromatic and is substituted with at least one functional group.
9. The process of any preceding claim wherein the organometallic compound is an alkoxy silane, silane, silazone or phenyl siloxane.
10. The process of any preceding claim wherein the organometallic compound is hexamethyldisiloxane.
11. The process of any preceding claim wherein the surface energy is between 18 and 50 mJ/m².

-22-

12. The process of any preceding claim wherein the organometallic compound is contacted with metal surface in the liquid phase, gaseous phase or mixed liquid-gaseous phase in the presence of a carrier fluid.

13. The process of any preceding claim wherein the layer of organometallic molecules is from 1 to 3 molecular layers thick.

14. The process of claims 1 or 2 wherein the temperature is less than 400°C.

15. A metal surface capable of resisting fouling when exposed to corrosive or coke forming at atmospheric or greater pressures which comprises a metal surface and a layer of organometallic molecules deposited on said metal surface, said layer of organometallic molecules being 1 to 10 molecular layers thick, which layer will not undergo substantial decomposition at temperatures up to 450°C, which layer has a surface energy lower than 50 millijoule/m².

16. The metal surface of claim 15 wherein the layer of organometallic molecules is deposited on 80 to 100 % of the metal surface.