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Clavenna et al.(10) **Pub. No.: US 2008/0073063 A1**(43) **Pub. Date: Mar. 27, 2008**(54) **REDUCTION OF FOULING IN HEAT EXCHANGERS**(75) Inventors: **LeRoy R. Clavenna**, Baton Rouge, LA (US); **Ian A. Cody**, Annandale, NJ (US); **Ashley E. Cooper**, Baton Rouge, LA (US); **Steve Colgrove**, Baton Rouge, LA (US); **Hugh L. Huffman**, Lexington, KY (US); **Julio D. Lobo**, Alexandria, VA (US); **Limin Song**, West Windsor, NJ (US); **H. Alan Wolf**, Morristown, NJ (US); **Glen B. Brons**, Phillipsburg, NJ (US); **George A. Lutz**, Brick, NJ (US); **Mohsen S. Yeganeh**, Hillsborough, NJ (US)

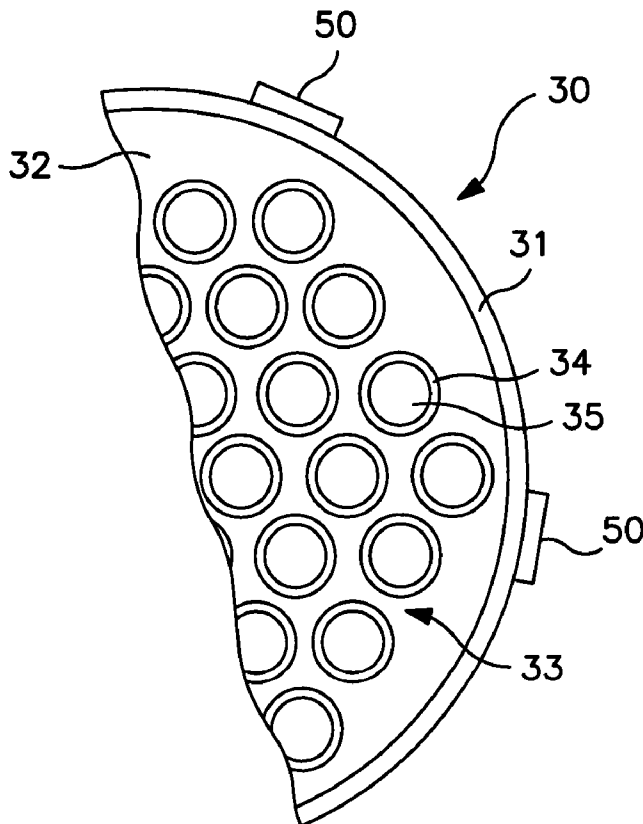
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Annandale, NJ 08801-0900 (US)(73) Assignee: **ExxonMobil Research and Engineering Company**, Annandale, NJ (US)(21) Appl. No.: **11/802,617**(22) Filed: **May 24, 2007****Related U.S. Application Data**

(60) Provisional application No. 60/815,845, filed on Jun. 23, 2006.

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F28F 19/02 (2006.01)
(52) **U.S. Cl.** **165/84; 165/133**(57) **ABSTRACT**

A method for reducing the formation of deposits on the inner walls of a tubular heat exchanger through which a petroleum-based liquid is flowing comprises applying one of fluid pressure pulsations to the liquid flowing through the tubes of the exchanger and vibration to the heat exchanger to effect a reduction of the viscous boundary layer adjacent the inner walls of the tubular heat exchange surfaces. Reduction of the viscous boundary layer at the tube walls not only reduces the incidence of fouling with its consequential beneficial effect on equipment life but it also has the desirable effect of promoting heat transfer from the tube wall to the liquid in the tubes. Fouling and corrosion are further reduced by the use of a coating on the inner wall surfaces of the exchanger tubes.



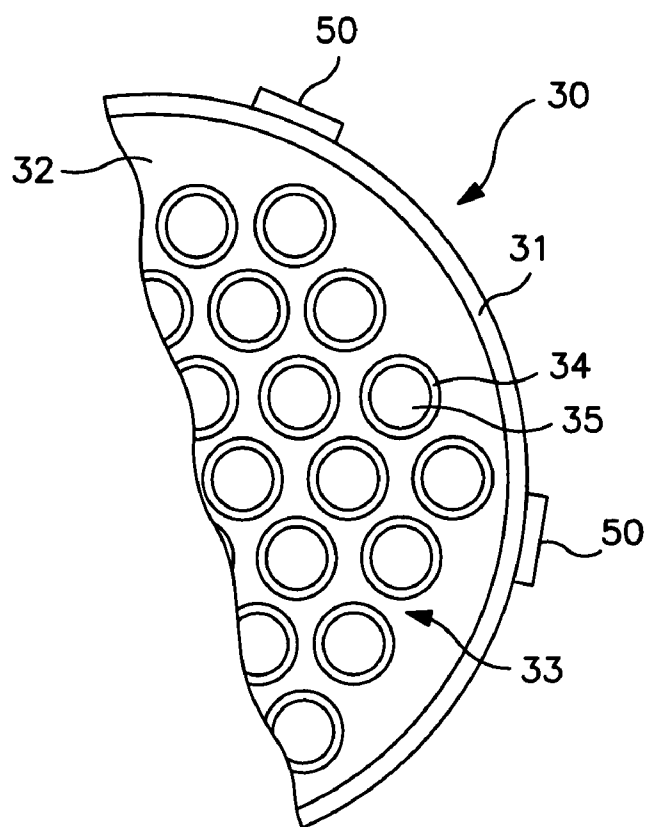


FIG. 1

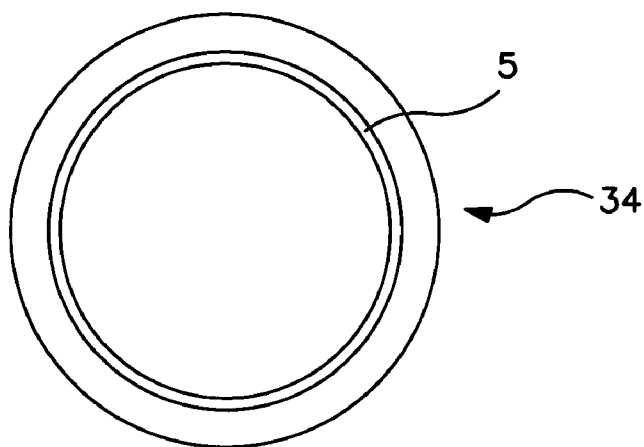


FIG. 2

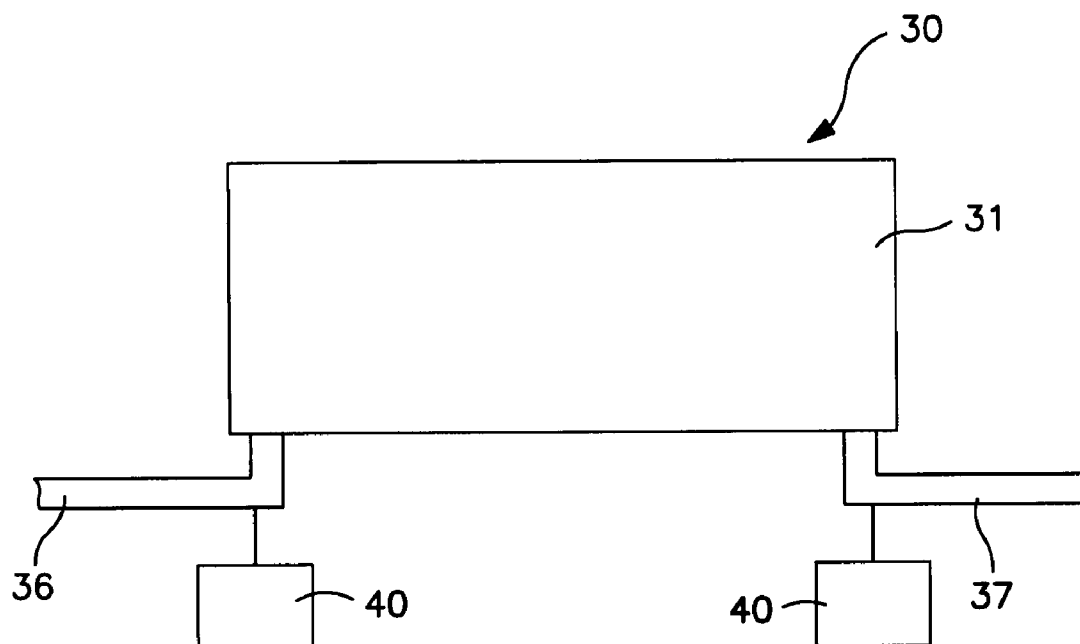


FIG. 3

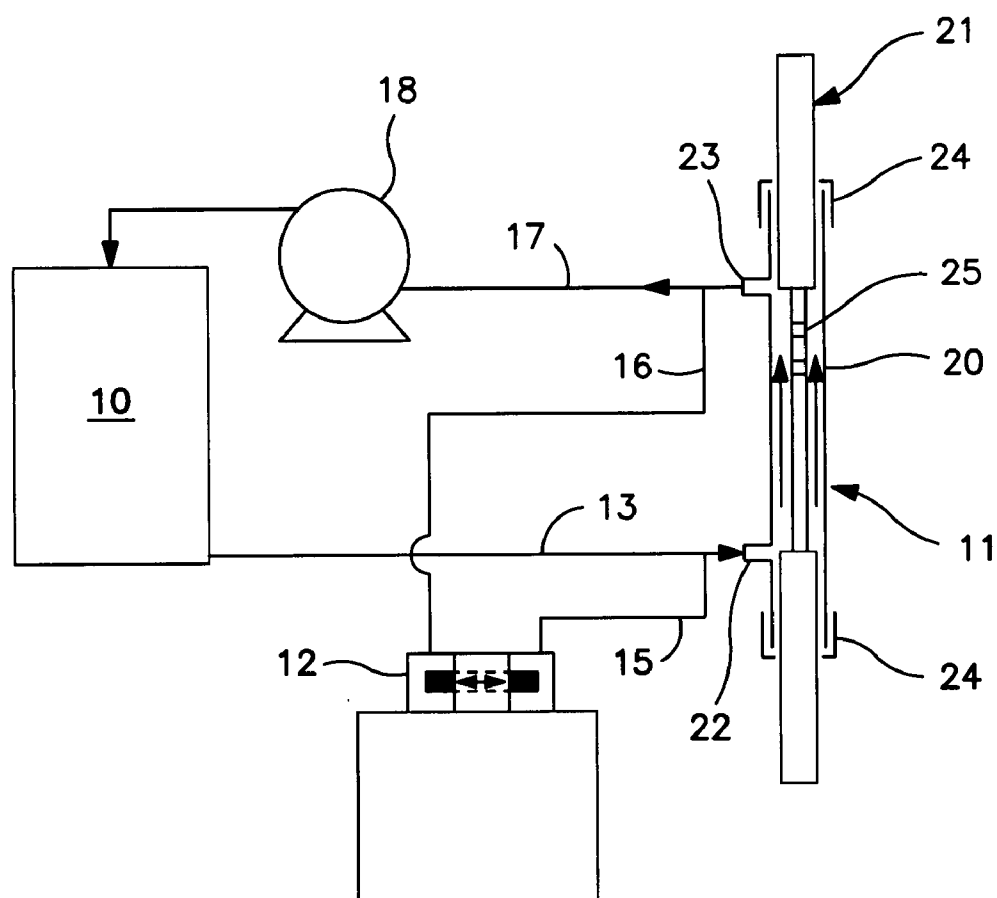


FIG. 4

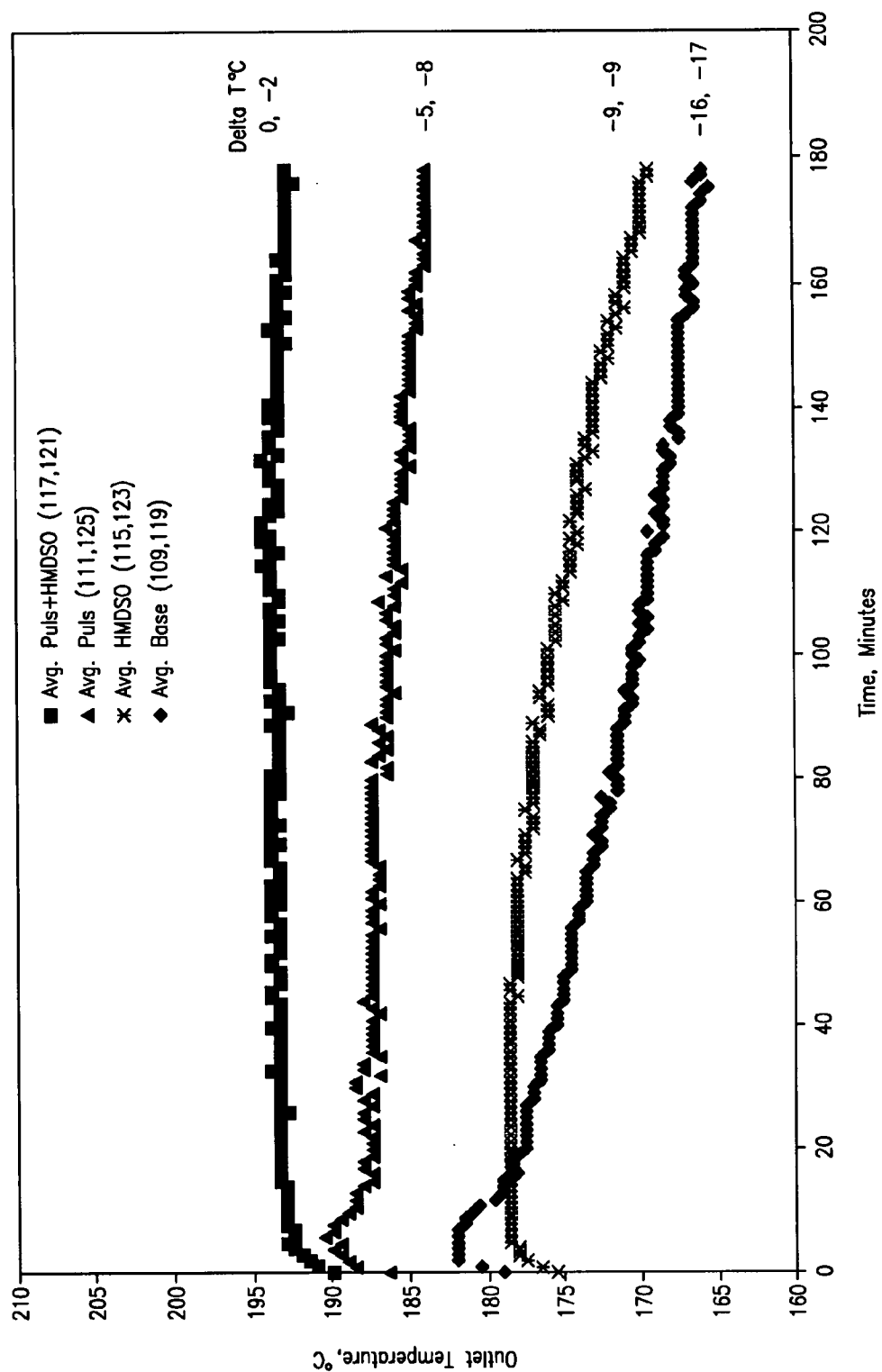


FIG. 5

REDUCTION OF FOULING IN HEAT EXCHANGERS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application relates and claims priority from U.S. Provisional Patent Application No. 60/815,845, filed on Jun. 23, 2006, entitled "Reduction of Fouling in Heat Exchangers."

[0002] This application also relates to co-pending U.S. patent application Ser. No. 11/304,874, which describes a method of applying low surface energy coatings to heat exchanger surfaces to reduce corrosion and the incidence of fouling on the surfaces, co-pending U.S. Patent Application Ser. No. 60/751,985, which describes a corrosion resistant material for reduced fouling in heat exchangers and methods for making coatings of such materials, and co-pending U.S. patent application Ser. No. 11/436,802, which describes a method of reducing fouling in heat exchangers by applying a mechanical force to the heat exchanger to induce vibration in the heat exchanger, which causes a shear motion in the liquid flowing within the heat exchanger.

FIELD OF THE INVENTION

[0003] This invention relates to the reduction of fouling in heat exchangers. This invention also relates to a process and an apparatus for preventing the deposition of solid matter on the internal walls of heat exchangers.

BACKGROUND OF THE INVENTION

[0004] Heat exchangers are well known and widely used in the chemical process industries and in petroleum refining. Heat exchangers have a tendency to become fouled by deposits of solid material, necessitating occasional removal from service for cleaning. Fouling in heat exchangers used for petroleum type streams can result from a number of mechanisms including chemical reactions, corrosion, deposit of insoluble materials, and deposit of materials made insoluble by the temperature difference between the fluid and heat exchange wall. Two important fouling mechanisms are chemical reactions and the deposition of insoluble materials. In both fouling mechanisms, the reduction of the viscous sub-layer (or boundary layer) close to the wall can mitigate the fouling rate. In the case of chemical reactions, the high temperature at the surface of the heat transfer wall activates molecules to form precursors for the fouling residue. If these precursors are not swept out of the relatively stagnant wall region they will associate together and deposit on the wall. A reduction of the boundary layer reduces the thickness of the stagnant region and hence the amount of precursors available to form a fouling residue. In the case of the deposition of insoluble materials, a reduction in the boundary layer increases the shear near the wall and hence exerts a greater force on the insoluble particle near the wall to overcome the particle's attractive forces to the wall and hence reducing its probability of deposition and incorporation into the fouling residue.

[0005] When the walls of a heat exchanger become coated with deposits, a number of difficulties ensue: (i) the heat transfer rate between the tube wall and the material in the tube diminishes; (ii) temperature regulation deteriorates, (iii) overheating often develops in the tubing, leading to short-

ened equipment life; (iv) shut-downs and cleaning cycles are necessary, and the longer the exchanger tubing, the more expensive and difficult is the cleaning job; (v) damage to the exchanger or ancillary equipment results when reactor tubes become plugged and relief valves burst. Fouling costs petroleum refineries significant amounts of money each year due to lost efficiencies, lost throughput, and waste of energy. The current method used to maintain heat exchanger efficiency is to periodically bring the heat exchanger out of service to clean it by chemical or mechanical methods. This can be costly and labor intensive. This adds significantly to the maintenance cost of the equipment and often requires replacement of the major components. This downtime and the costs of unexpected/unplanned shutdowns also add to the costs associated with fouling.

[0006] U.S. Pat. No. 4,271,007 to Souhrada, in dealing with deposit formation in tubular reactors, mentions a number of methods for preventing deposit formation including the control of reaction conditions, adjustment of the feed rate of any catalyst to avoid rapid reaction and consequent overheating, the addition of inhibiting chemicals, the use of liquid curtains or oil films to prevent solid materials from contacting the reactor walls, and recycling a portion of the product from a reactor to the inlet, to increase the linear flow rate in the reactor and maintain turbulent flow conditions. Mention is also made that deposits may be removed by mechanical means including high pressure water or steam jets, by solvents or by chemical reaction. All these procedures, however, require removing part or all of the reactor from service for the cleaning cycle and the same would apply equally to heat exchanger service with their concomitant losses in equipment utilization rates as well as an undesirable labor burden.

[0007] U.S. Pat. No. 3,183,967 to Mettenleiter proposes reducing the formation of sediment and scaling on the walls of heat exchanger tubing by mounting the tubing header resiliently or flexibly at one or both ends of the tube bundle and applying vibration at predetermined intervals to repel solids from the walls of the tubes. Arrangements of this type are, however, mechanically complicated and add significant cost to the design of what would otherwise be a relatively inexpensive device which normally contains no moving parts.

[0008] In practical terms, the reduction of scale or deposit formation by the use of mechanically applied vibration, as described in Mettenleiter, by the use of flexible mounted tube bundles with mechanical shakers or rappers has not achieved any significant acceptance with heat exchangers. A different approach using fluid pressure pulsations to clean fouled heat exchanger surfaces has been described in U.S. Pat. No. 4,645,542 to Scharton, U.S. Pat. No. 4,655,846 to Scharton and U.S. Pat. No. 5,674,323 to Garcia but all these proposals have the marked disadvantage of requiring the equipment to be taken out of service and subjected to the cleaning procedure. The same is true of the sonic cleaning method described in U.S. Pat. No. 4,461,651 to Hall. The use of flow oscillations in a liquid reactant flowing through a reactor such as a polymerization or cracking reactor for checking the deposition of solids on the reactor walls in described in Sourhada and in a similar vein, U.S. Pat. No. 3,819,740 to Saburo Hori proposes the use of an ultrasonic wave generator for inhibiting the accumulation of coke deposits on the walls of thermal cracking reactors. U.S. Pat.

No. 5,287,915 to Liu describes a method of removing deposits from the walls of heat exchangers used for cooling hot gases, e.g. in the production of synthesis gas, by forming the heat exchanger tube into a moveable configuration such as a coil which can then be vibrated or shaken by the use of electrodynamic, hydraulic or mechanical means. One possibility referred to is to use the water hammer effect to vibrate a coil type exchanger, creating the water hammer by sudden changes in the flow rate of the coolant in the tube.

[0009] There have been prior attempts at using coatings on the surfaces of heat exchanges to reduce corrosion. These attempts are not effective in reducing fouling. One, for example, intended for forming a protective surface film functions 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 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.

[0010] Other coatings are based on polymeric materials such as polyethylene and polyvinylfluoride with low surface energy such as the coatings used to inhibit biofouling in aqueous environments at ambient conditions. These polymeric coatings generally cannot withstand higher temperature conditions typical of refinery operations and are not effective to reduce hydrocarbon fouling adequately.

[0011] 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. Coatings of such thickness may, however, limit heat transfer. 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. The use of silanes for chemical vapor deposition is 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. Thus, conventional treatments tend to be inadequate either because they are too thick for good heat transfer or, alternatively, do not adequately resist fouling.

[0012] There is a need to reduce and/or eliminate fouling in heat exchangers, which is presently not addressed by the prior art.

SUMMARY OF THE INVENTION

[0013] It is an aspect of the present invention to combine pulsation or vibration, which reduces the amount of available foulants, with surface treatment, which reduces the probability of the foulant adhering to the surface. The resulting combination achieves a reduction of fouling that is

greater than either method when used separately. This can result in significant cost savings because of the extended time period between cleaning of the heat exchanger and the overall increased heat exchanger efficiency and, in so doing, can minimize or prevent fouling of heater tubes which will increase run lengths between turnarounds, avoid unplanned shutdowns, avoid replacement of process tubes, improve overall operations reliability and reduce the cost of decoking.

[0014] According to the present invention, the method for reducing the formation of deposits on the walls of a heat exchanger through which a petroleum-based liquid is flowing, comprises applying one of fluid pressure pulsations and vibration to the liquid flowing through the exchanger to effect a reduction of the viscous boundary layer adjacent the walls of the heat exchange surface. The walls of the heat exchange surfaces are coated with a low surface energy material to which the expected deposits are non-adherent so that the possibility of fouling is reduced further to an extent that is not achievable by either expedient on its own.

[0015] The present invention therefore provides an improvement to a heat exchanger which is used for effecting heat exchange between a petroleum-based liquid and a heat exchange medium which flows on an opposite side of a heat exchange surface to the liquid. It is an aspect of the present invention to reduce fouling in the exchanger on the side of the heat exchange surface in contact with the liquid by applying fluid pressure pulsations to the petroleum liquid flowing through the exchanger or vibration to the heat exchange unit to effect shear motion in the petroleum liquid flowing through the exchanger to effect a reduction of the viscous boundary layer adjacent the walls of the heat exchange surface in contact with the liquid so as to reduce the incidence of fouling and promote heat transfer from the wall to the liquid. The wall of the heat exchange surface, e.g. the inner wall of the tube, which in contact with the liquid is selected as one which has an adherent, fouling resistant coating having a low surface energy (e.g., not more than 50 mJ/m²). The combination of pulsation or vibration with a low surface energy fouling resistant coating is effective in reducing fouling, which improves heat transfer. The particles that cause fouling are less likely to adhere to the low energy surface due to lower adhesion strengths. The use of pulsation or vibration creates oscillating shear stresses adjacent the walls of the exchanger and is effective in removing the foulant particles from the wall of the exchanger surfaces. The oscillating shear stresses act to tear or pull the loosely adhered particles from the surfaces.

[0016] The principles of the present invention can be applied to new heat exchangers or to retrofit an existing heat exchanger by connecting a fluid pressure pulsator or vibration producing device to side of the exchanger used for the petroleum liquid; again, the heat exchange surface walls in contact with the petroleum liquid are low-surface energy walls since these have been found to be the most effective in reducing fouling. As described below, a number of different fluid pulsator types may be used although positive-displacement reciprocating pumps and diaphragm pumps will be found to be efficacious for this purpose. Alternatively, it is also contemplated that a vibration producing device can be connected to the heat exchange unit to induce vibration in the heat exchange unit to affect shear motion in the petroleum liquid flowing through the heat exchange unit.

[0017] Reduction of the viscous boundary layer at the tube walls not only reduces the incidence of fouling with its consequential beneficial effect on equipment life but it also has the desirable effect of promoting heat transfer from the tube wall to the liquid in the tubes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] The invention will now be described in conjunction with the accompanying drawings in which:

[0019] FIG. 1 is a partial cross-sectional view of a shell and tube heat exchanger in accordance with an embodiment of the present invention;

[0020] FIG. 2 is a cross-sectional view of a heat exchanger tube of FIG. 1 illustrating the coating in accordance with the present invention;

[0021] FIG. 3 is a schematic view of a heat exchanger in accordance with another embodiment of the present invention;

[0022] FIG. 4 is a simplified equipment schematic of a test rig for demonstrating the application of the present invention to a heat exchanger; and

[0023] FIG. 5 is a graphical representation of the results achieved in the testing reported below.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The present invention will now be described in greater detail in connection with the attached figures. FIG. 1 is a tube-in-shell heat exchanger 30, which is located upstream from a furnace (not shown) and employs the principles of the present invention. The tube-in-shell heat exchanger 30 disclosed herein illustrates one application of the present invention to reduce sulfidation or sulfidic corrosion and depositional fouling in refinery and petrochemical applications. The tube-in-shell exchanger 30 is just one heat transfer component falling under the scope of the corrosion reduction and fouling mitigation measures in accordance with the present invention. The principles of the present invention are intended to be used in other heat exchangers including but not limited to spiral heat exchangers, tube-in-tube heat exchangers and plate-and-frame heat exchangers having at least one heat transfer element. The principles of the present invention are intended to be employed in other heat transfer components including furnaces, furnace tubes and other heat transfer components which may be prone to petroleum and/or vacuum residual fouling.

[0025] The heat exchanger 30 is used to pre-heat crude oil in a refinery operation prior to entry into the furnace. The heat exchanger 30 includes a housing or shell 31, which surrounds and forms a hollow interior 32. A bundle 33 of heat exchanger tubes 34 is located within the hollow interior 32, as shown in FIG. 1. The bundle 33 includes a plurality of tubes 34. The tubes 34 may be arranged in a triangular configuration or a rectangular configuration. Other tube arrangements are contemplated and considered to be well within the scope of the present invention. Each tube 34 has a generally hollow interior 35 such that the crude oil to be heated flows there-through. The heating or warming fluid (e.g., vacuum residual stream) flows through the hollow

interior 32 to pre-heat the crude oil stream as the stream flows through the hollow interior 35 towards the furnace. Alternatively, it is contemplated that the crude oil may flow through the hollow interior 32 of the housing 31.

[0026] Most heat exchangers are constructed from carbon steel for reasons of cost possibly with tubes of copper, copper alloys, brass (including muntz metal), cupronickel, stainless steel, admiralty metal, aluminum or bronze (including aluminum bronzes and nickel aluminum bronzes) but in principle, the present invention may be applied to exchangers regardless of the construction material although suitable choice of non-adherent coating material will be required appropriate to the selected construction material.

[0027] The principal advantage of the present invention is that it can be readily adapted for use in existing heat exchange equipment. No mechanical modifications to the actual heat exchange unit are required since the pressure pulsations may be applied to the liquid flow stream in the exchanger tubes 34 by an external mechanism. For example, a pulsation device 40 may be coupled to the liquid inlet conduit 36 or liquid outlet conduit 37 (or both) on the tube side of the exchanger 30, as shown in FIG. 3. As described below in reference to the test rig used to validate the performance of the invention, the fluid pulsation device 40 may be connected across the exchanger, to provide pressure-balance positive pulsation on one side of the exchanger with a negative pulsation on the other side so as not create undesirable pressure excursions within the exchanger itself. Alternatively, a single pulsator may be used, normally on the inlet side, with a valve on the outlet side, if necessary, to relieve any excess pressures created by the pulses.

[0028] Like pressure pulsations, no internal modifications to the heat exchange unit are required when vibration is applied to the heat exchange unit. External units 50 may be connected to the heat exchange unit to induce vibration creating the shear motion in the liquid flow stream, as disclosed in co-pending U.S. patent Ser. No. 11/436,802, entitled "Mitigation of In-Tube Fouling in Heat Exchangers Using Controlled Mechanical Vibration", the disclosure of which is specifically incorporated herein by reference.

[0029] The present invention is applicable to use in heat exchangers operating with a wide variety of liquids on the tube side of the exchanger where a tendency to form deposits in the tubes is a potential source of trouble, for example, water-based liquids including emulsions and unstable solutions and oily liquids such as petroleum-based liquids, e.g. crude oil, reduced crudes, heavy refinery streams such as delayed coker feed, coker heavy gas oil, visbreaker feed, vacuum gas oil, aromatic extract, and the like. It is with petroleum feeds that the present invention is particularly useful.

[0030] The pulsation device 40 will comprise any means for applying liquid pressure pulsations to the tube side liquid. In the simplest concept, the device may comprise a reciprocating pump type mechanism with a cylinder connected to the inlet/outlet conduits of the exchanger and a reciprocating piston in the cylinder to vary the internal volume of the cylinder. As the piston moves within the cylinder, the liquid will alternately be drawn into the cylinder and then expelled from it, creating pulsations in the conduit to which the device is connected. The use of a double-acting pump of this kind with one side connected to

the inlet conduit and the other connected to the outlet conduit is particularly desirable since it will create the desired pressure pulsations in the tubes regardless of the pressure drop occurring in the exchanger tube bundle. Variation in the frequency of the pulsations may be afforded by variations in the reciprocation speed of the piston and any desired variations in pulsation amplitude may be provided by the use of a variable displacement pump, e.g. a variable displacement piston pump, swashplate (stationary plate) pump and its variations such as the wobble plate (rotary plate) pump or bent axis pump.

[0031] Other types of pumps may also be used as the pulsation device including diaphragm pumps and these may be practically attractive since they offer the potential for activation of the diaphragm by electrical, pneumatic or direct mechanical means with the movement of the diaphragm controlled to provide the desired frequency and amplitude (by control of the extent of diaphragm movement). Other types may also be used but gear pumps and related types such as the helical rotor and multi screw pumps which give a relatively smooth (non pulsating) fluid flow are less preferred in view of the objective of introducing pulsations which disrupt the formation of the troublesome boundary layer. Other types which do produce flow pulsations such as the lobe pump, the vane pump and the similar radial piston pump, are normally less preferred although they may be able to produce sufficient pulsation for the desired purpose. Given the objective is to induce pulsations, other types of pulsator may be used, for example, a flow interrupter which periodically interrupts the liquid flow on the tube side. Pulsators of this type may include, for example, siren type, rotary vane pulsators in which the flow interruption is caused by the repeated opening and closing of liquid flow passages in a stator/rotor pair, each of which has radial flow openings which coincide with rotation of the moving rotor member. The rotor may suitably be given impetus by the use of vanes at an angle to the direction of liquid flow, e.g. by making radial cuts in the rotor disc and bending tabs away from the plane of the disc to form the vanes. Another type is the reed valve type with spring metal vanes which cover apertures in a disc and which are opened temporarily by the pressure of the fluid in the tube, followed by a period when the vane snaps closed until fluid pressure once more forces the vane open.

[0032] As shown in FIG. 3, the pulsation device 40 is preferably located close to the exchanger in order to ensure that the pulsations are efficiently transferred to the liquid flow in the tube bundle, that is, the pulsations are not degraded by passage through intervening devices such as valves. Normally, the frequency of the liquid pulsations will be in the range of 0.1 Hz to 20 kHz. The amplitude of the pulsation as measured by the incremental flow rate through the heat exchange tubes could range from about the order of the normal heat exchanger flow rate at the lower end of the range of pulsation frequencies to less than 10^{-6} of the normal heat exchanger flow rate at the higher frequencies; because of pressure drop limitations in the heat exchanger operation and/or dissipation of higher frequencies in the fluid, the upper limit of the pulse amplitude will decrease with increased frequency. Thus, for example, in the lower half of this frequency range, the amplitude of the pulsations could be from about 10^{-2} to about the normal flow rate and with frequencies in the upper half of the range, from about 10^{-6} to 0.1 of the normal flow rate through the exchanger.

[0033] Alternatively, a vibration producing device 50 may be used instead of the liquid pulsation device, described above. The vibration producing device may be of the kind disclosed in co-pending U.S. patent Ser. No. 11/436,802. The vibration producing device may be externally connected to the heat exchange unit to impart controlled vibrational energy to the tubes of the bundle. The vibration producing device 50 can take the form of any type of mechanical device that induces tube vibration while maintaining structural integrity of the heat exchanger. Any device capable of generating sufficient dynamic force at selected frequencies would be suitable. The vibration producing device can be single device, such as an impact hammer or electromagnetic shaker, or an array of devices, such as hammers, shakers or piezoelectric stacks. An array of devices 50 can be spatially distributed to generate the desired dynamic signal to achieve an optimal vibrational frequency, as shown in FIG. 1. The vibration producing device may be placed at various locations on or near the heat exchange unit as long as there is a mechanical link to the tubes.

[0034] Sufficient vibration energy can be transferred from the tubes of the heat exchanger at vibration modes. There are low and high frequency vibration modes of tubes. For low frequency modes (typically below 1000 Hz), axial excitation is more efficient at transmitting vibration energy, while at high frequency modes, transverse excitation is more efficient. The density of the vibration modes is higher at a high frequency range than at a low frequency range (typically below 1000 Hz), and vibration energy transfer efficiency is also higher in the high frequency range. Further, displacement of tube vibration is very small at high frequency (>1000 Hz) and insignificant for potential damage to the tubes.

[0035] The use of vibration or pulsation reduces fouling in the heat exchanger by creating oscillating shear stresses adjacent the walls of the exchanger that reduce the boundary layers adjacent the exchanger surfaces. These oscillating shear stresses when combined with a low surface energy fouling resistant coating are effective in reducing fouling because the fouling particles can be removed from the heat exchanger surfaces. The oscillating shear stresses act to tear or pull the loosely adhered particles from the surfaces.

[0036] As noted above, many coatings of the conventional type, for example, epoxies, tend to be relatively thick with a consequent adverse effect on heat transfer and for this reason, coating methods which result in a relatively thin thickness of coating, desirably no more than 10 molecular layers thick, are preferred provided that the necessary characteristics of corrosion and fouling resistance are achieved. The gas phase and vapor deposition methods are therefore likely to comment themselves for this purpose.

[0037] A preferred class of coatings are the low surface energy coatings described in co-pending U.S. patent application Ser. No. 11/304,874, to which reference is made for a description of such coatings, their properties and methods of applying them to heat exchanger surfaces. These coatings are constituted by a layer of organometallic molecules which is 1 to 10 molecular layers thick which will not undergo substantial decomposition at temperatures up to 450° C. and which has a surface energy lower than 50 millijoule/m². The coatings are applied by contacting the metal surface with an organometallic compound capable of bonding to the metallic

surface to form the desired surface layer. It is preferred to prepare the metal surface prior to treatment by heating the metal surface in an oxygen-containing atmosphere at temperatures of from 100° C. to 500° C. to clean said metal surface of any carbonaceous residues and then contacting the metal surface with the requisite organometallic compound.

[0038] Alternative low energy surface coatings which inhibit the deposition of fouling deposits are the coatings produced by the processes known as Hollow Cathode Plasma Immersion Ion Processing or the plasma-assisted chemical vapor deposition (PACVD) process, both of which are commercially available processes (from the Bekaert Company) which produce coatings referred to as "Diamond-like Coatings". Diamond-like Coatings are amorphous carbon based coatings with a high hardness and a low coefficient of friction. Their composition and structure results in excellent wear resistance and non-sticking characteristics. These coatings are thin, chemically inert and have a low surface roughness. They can be tailored to have a wide range of electrical resistivity with a standard thickness between 0.002 and 0.04 mm. Compositionally, the carbon Diamond-like Coatings are a mixture of sp² and sp³ bonded carbon atoms with a hydrogen concentration between 0-80%. These coatings provide high hardness and abrasion resistance characteristics. Diamond-like Composite Coatings comprising C, H, Si and O are also available. Phosphate and phosphite ester coatings, and fluorinated surface coatings which may be applied in thin, adherent layers, which can also be produced by commercially available processes are also potentially applicable.

[0039] The organometallic compounds used to form the preferred low energy coatings described in application Ser. No. 11/304,874 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 case of the preferred low energy coatings, the organometallic compound, not its oxide, functions as the protective coating. Thus, the organometallic coating functions as a chemical protective layer in the monolayer range as compared to a physical barrier provided by thicker coatings.

[0040] In the organometallic compounds used as coating materials, the metallo components of the organometallic compounds are selected from Groups 4 to 15 based on the IUPAC format for the Periodic Table having Groups 1 to 18, and are preferably selected from 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.

[0041] The organometallic coating on the metallic surface should preferably have a low energy surface, that is, a surface free energy lower than 50 milliJoules/square meter (mJ/m²), preferably between 21 to 45 mJ/m². 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. Thermally conductive, adherent, corrosion-resistant layers such as the ones produced by electropolishing and as described below, can be used as substrates for the superficial molecular layer-thick coating. Reference is made to Application Ser. No. 60/751,985, "Corrosion Resistant Material For Reduced Fouling, A Heat Exchanger Having Reduced Fouling And A Method For Reducing Heat Exchanger Fouling In A Refinery") for a more detailed description of these methods.

[0042] The surface free energy of the coating can be determined by measuring the water contact angle. Similarly, the extent of the surface modification by the 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 modified metal surfaces, measured water contact angles are between 95° to 160°, preferably 110° to 150°, with angles of at least 130° giving best results.

[0043] The amount of covering of the organometallic coating layer ranges from greater than 25% with, of course, correspondingly better resistance to corrosion and fouling as the covering of the metal surface approaches 100% of the metal surface. Thus, from 50 to 100% is preferably covered, more preferably from 80 to 100% and for optimal results, 100% or as close to 100% as possible.

[0044] 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 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 corrosion resistance as well as the effectiveness of the organometallic coating process. For example, a carbon steel surface may be first treated with a chromium salt solution to form a chromium-rich surface

layer. Chromium-enhanced surface layers may be produced by electro-polishing the tube in a solution containing chromic acid. This is effective to increase the chromium concentration at the surface when the chromium content in the substrate steel is less than about 15 wt. %. The electropolishing technique is also particularly advantageous because it is capable of producing a surface with a surface roughness of less than 1000 nm, preferably less than 500 nm and more preferably less than 250 nm, which, when given a superficial organometallic coating is well able to resist fouling deposits and corrosion. The chromium-enriched layer may also be formed using various other techniques including electroplating chromium onto another alloy such as a carbon steel, thermal spray coating, laser deposition, sputtering, physical vapor deposition, chemical vapor deposition, plasma powder welding overlay, cladding, and diffusion bonding. It is also possible to choose a high chromium alloy such as 316 stainless steel. The chromium-enhanced layer may be mechanically polished and/or electro-polished as described above to obtain a uniform surface roughness within the desired range.

[0045] The chromium-enriched layer may be given a superficial oxide layer prior to deposition of the organometallic coating. The oxide layer will typically include an oxide species whose own composition will be dependent on the metallurgy of the substrate; thus, with ferrous metal tubes, the oxide layer may typically be expected to include one or more of magnetite, iron-chromium spinels and chromium oxides.

[0046] Various other techniques may also be used for the generation of chromium-enriched surface layers on the exchanger tubes including, but not limited to electroplating, thermal spray coating, laser deposition, sputtering, physical vapor deposition, chemical vapor deposition, plasma powder welding overlay, cladding, and diffusion bonding. Passivation, that is treatment of metals with dilute nitric or citric acid, for example, can also be used to increase the concentration of chromium at the surface when working with stainless steel alloys. The combination of electropolishing and passivation is also a useful method for achieving this effect.

[0047] The organometallic coating can be formed on the cleaned and heated metal surface by exposing the heated metal to the selected organometallic compound in the gaseous phase, liquid phase or mixed liquid-vapor phase. The organometallic compound may, for example, be sparged into the vapor state using a carrier gas such as nitrogen or it 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 suitably 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.

[0048] 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.

[0049] A coated heat exchanger tube 34 is illustrated in cross-section in FIG. 3. In this case, the coating 5 is located on the inside of the tube 34 consistent with the possibility that fouling is expected on that side with a non-fouling medium on the shell side. If, however, fouling were to be expected on the shell side, the coating could be applied to that side or even to both sides if necessary. The coating 5 extends over the inner surface of tube 34 to provide resistance to fouling but in this case, this resistance is enhanced by the use of the fluid pulsation technique to provide superior anti-fouling performance.

[0050] 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.

[0051] The behavior of the present organometallic coatings is believed to be at least in part a function of the organo moiety. 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 organometallics because their 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 ferrous metal alloys, 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.

[0052] To determine the effect of fluid pulsation on fouling, a pulsation flow unit was added to an Alcor™ HLPS-400 Liquid Process Simulator. The resulting test rig is shown in FIG. 4. The Alcor HLPS-400 Hot Liquid Process Simulator is a laboratory tool for predicting heat exchanger performance and the fouling tendencies of specific process fluids. The Alcor HLPS operates in the laminar flow regime at accelerated fouling conditions compared to commercial heat exchangers which typically operate a high turbulent flow regime at much lower fouling rate but in spite of these differences, the Alcor HLPS has proven to be an excellent tool for predicting the relative fouling tendencies of fluids in commercial heat exchangers.

[0053] For this fouling study a crude oil was run in the Alcor HLPS. The basic Alcor HLPS consists of a crude sample reservoir 10, a heat exchanger test section 11 and a constant displacement pump 12 located downstream of the

test section. The test oil is pumped in a closed cycle from reservoir **10** through line **13** to test section **11**. A branch line **15** passes from line **13** to one side of a the positively driven, double acting, reciprocating displacement pump **12** which was a dual head Constametric™ HPLC metering pump modified by removing the check valves from each pump head and closing the inlet to the pump heads. In a similar manner, branch line **16** extends from oil return line **17** to the other side of pump **12**. Circulating pump **18** of the constant displacement type maintains the oil in circulation during the test run in a closed cycle from the reservoir, through the test section and then back to the reservoir. Test section **11** comprises a cylindrical tube casing **20** which surrounds a centrally located test coupon in the form of a rod **21** with a narrowed center section **25** within the tubular casing. The tubular casing has a liquid inlet port **22** connected to feed line **13** and an outlet port **23** connected to return line **17**. Liquid seal between the coupon and the casing is provided by gaskets at each end with end caps **24** where the coupon exits the casing; the gaskets also insulate the coupon electrically from the outer casing. The coupon may be heated electrically by means of electrical connections (not shown) at its two ends, connected to a controller to supply current at various amperages depending on the degree of heating required. In this test program, the coupon is used as a surrogate for a heat exchanger tube.

[0054] The test run time was for three hours with additional fifteen minute periods for each heat-up and cool-down. Tests were carried out by charging a reservoir with 800 ml of the test crude. The crude in the reservoir and lines to and from the test heat exchanger were heated to 150° C. To prevent vaporization of the test fluid, the system was pressurized to approximately 3450 kPag (500 psig) with nitrogen. The fluid from the reservoir was pulled through the test heat exchanger by the downstream constant displacement circulation pump at a flow rate of 3 ml/min. which returned the fluid to the top of the reservoir. A piston was placed in the reservoir to separate the fresh crude from the used, heat exchanged crude. In the test heat exchanger, the fluid flows up through the annulus formed by a vertically positioned heated test coupon rod. The test section of the heated rod is about 3.20 mm in outside diameter and 60 mm long. The outer shell of the test heat exchanger has a 5.10 mm inside diameter forming a 0.95 mm annular space for flow. The temperature of the heated rod is controlled by a thermocouple located inside the heated rod test section, set to 275° C. in this study. The temperatures of the fluid to the inlet and from the outlet of the heat exchanger were recorded over the duration of the test. As deposits or fouling material builds up on the surface of the heated rod, the outlet temperature of the fluid from the heat exchanger decreases. This decrease results from the insulating nature of the deposit on the rod. The decrease in outlet temperature gives a measure of the fouling tendency of the fluid on the rod surface as well as of the heat transfer efficiency of the unit.

[0055] During operation the volume inside each head of the metering pump was varied by 0.10 ml; the changes in volume of the pump heads are approximately 180 degrees out of phase. In the pulsation tests, the pump speed was adjusted to give a fluid pulsation of 0.083 ml/sec in both the forward and reverse flow directions.

[0056] The coating used in this study was obtained by treating the Alcor rods with HMDSO (hexamethyldisilox-

ane). The Alcor rods used in this study were 1018 carbon steel. Because the new rods are coated with light oil, the rods were cleaned sequentially with toluene, iso-propyl alcohol (IPA), water, and then IPA to dry the rod. The clean rods were loaded in a horizontal, controlled atmosphere, alumina tube furnace. In the HMDSO treatment, the rods were first air oxidized at 350° C. for one hour, followed by purging the tube furnace with nitrogen for ten minutes, and then treating the rods with HMDSO vapor at 350° C. for one hour. The HMDSO vapor is carried to the furnace by bubbling nitrogen through a room temperature reservoir of HMDSO liquid. The Alcor rods are cooled under the HMDSO vapor before removal from the tube furnace. The effectiveness of the coating can be gauged the increase of the water contact angle. The clean rods had an average water contact angle of 81 degrees. After the HMDSO treatment, the rods made an average water contact angle of 129 degrees.

[0057] To examine the effect of liquid pulsation plus HMDSO treatment the following series of runs were made in the test unit: the base case with non-coated rods and no pulsation, the pulsation only case with the +/-0.083 ml/sec pulsation rate, the HMDSO treatment only case, and the pulsation plus HMDSO treatment case.

[0058] FIG. 5 shows the change in fouling obtained in the Alcor runs as depicted by decrease in outlet temperature. The average of two Alcor runs is shown for each case. The data curves in FIG. 5 show that the temperature decrease for the pulsation plus HMDSO treatment case is smaller compared to the base case indicating a lower fouling rate. The temperature decrease for the pulsation plus HMDSO treatment case is also smaller than either the pulsation only case or the HMDSO treatment case. This indicates a synergistic effect on reducing fouling when pulsation is combined with surface treatment. The starting temperature for the runs having pulsation are also shifted to higher temperature due to the enhanced heat transfer offered by the pulsation.

[0059] It will be apparent to those skilled in the art that various modifications and/or variations may be made without departing from the scope of the present invention. While the present invention has been described in the context of the heat exchanger in a refinery operation, the present invention is not intended to be so limited; rather, it is contemplated that the surface coatings and vibration and/or pulsation disclosed herein may be used in other portions of a refinery operation where fouling may be of a concern. Thus, it is intended that the present invention covers the modifications and variations of the method herein, provided they come within the scope of the appended claims and their equivalents.

What is claimed is:

1. A method for reducing the formation of deposits on walls of tubes in a heat exchanger through which a petroleum-based liquid is flowing, comprising:

applying one of fluid pressure pulsations to the liquid flowing through the tubes of the exchanger and vibration to the heat exchanger, wherein the wall contacting the liquid having an adherent fouling resistant coating having a surface energy of not more than 50 mJ/m².

2. A method according to claim 1, wherein mechanical vibration is applied to the heat exchanger.

3. A method according to claim 1, wherein fluid pulsation area applied to the liquid flowing through the tubes.

4. A method according to claim 3, wherein the fluid pressure pulsations are applied at a frequency in the range of 0.1 Hz to 20 kHz.

5. A method according to claim 3, wherein the amplitude of the pulsations as measured by the incremental flow rate through the heat exchange tubes is in the range from about 10^{-6} of the normal heat exchanger flow rate to about an order of the normal heat exchanger flow rate.

6. A method according to claim 5, wherein the pulsations are applied at a frequency in the range from 0.1 to 10 kHz and the amplitude of the pulsation as measured by the incremental flow rate through the heat exchange tubes is in the range of about 10^{-2} of the normal heat exchanger flow rate to about the order of the normal heat exchanger flow rate.

7. A method according to claim 5, wherein the pulsations are applied at a frequency in the range from 10 to 20 kHz and the amplitude of the pulsation as measured by the incremental flow rate through the heat exchange tubes is in the range of about 10^{-6} of the normal heat exchanger flow rate to about 0.1 of the order of the normal heat exchanger flow rate.

8. A method according to claim 1, wherein the adherent fouling resistant coating on the wall of the tubes comprises:

a layer of organometallic molecules having a thickness of 1 to 10 molecular layers, wherein the layer will not undergo substantial decomposition at temperatures up to 450° C., and wherein the layer has a surface energy lower than 50 millijoule/m².

9. A method according to claim 8, wherein the layer of organometallic molecules is deposited on 80 to 100% of the inner wall surface.

10. A method according to claim 8, wherein the metal in the organometallic compound is silicon.

11. A method according to claim 8, wherein the organo moiety in the organometallic compound is a hydrocarbyl group from 1 to 30 carbon atoms.

12. A method according to claim 11, wherein the hydrocarbyl group is aliphatic or aromatic and is substituted with at least one functional group.

13. A method according to claim 8, wherein the organometallic compound is an alkoxy silane, silane, silazone or phenyl siloxane.

14. A method according to claim 13, wherein the organometallic compound is hexamethyldisiloxane.

15. A method according to claim 8, wherein the surface energy of the coating is between 18 and 50 mJ/m².

16. A method according to claim 8, wherein the coating has a surface with a water contact angle from 95° to 160°.

17. A method according to claim 16, wherein the water contact angle is from 110° to 150°.

18. A method according to claim 16, wherein the water contact angle is from 130° to 160°.

19. A method according to claim 8, wherein mechanical vibration is applied to the heat exchanger.

20. A method according to claim 8, wherein fluid pressure pulsations are applied to the liquid flowing through the tubes.

21. A method according to claim 20, wherein the fluid pressure pulsations are applied at a frequency in the range of 0.1 Hz to 20 kHz.

22. A method according to claim 20, wherein the amplitude of the pulsations as measured by the incremental flow rate through the heat exchange tubes is in the range from

about 10^{-6} of the normal heat exchanger flow rate to about an order of the normal heat exchanger flow rate.

23. A method according to claim 22, wherein the pulsations are applied at a frequency in the range from 0.1 to 10 kHz and the amplitude of the pulsation as measured by the incremental flow rate through the heat exchange tubes is in the range of about 10^{-2} of the normal heat exchanger flow rate to about the order of the normal heat exchanger flow rate.

24. A method according to claim 22, wherein the pulsations are applied at a frequency in the range from 10 to 20 kHz and the amplitude of the pulsation as measured by the incremental flow rate through the heat exchange tubes is in the range of about 10^{-6} of the normal heat exchanger flow rate to about 0.1 of the order of the normal heat exchanger flow rate.

25. A heat exchanger for effecting heat exchange between a petroleum-based liquid and a heat exchange medium, comprising:

a housing having an interior;

a plurality of heat exchange tubes having a hollow interior passage for the passage of one of the petroleum-based liquid and the heat exchange medium therethrough, wherein each tube having an interior surface and an exterior surface;

an adherent fouling resistant coating on one at least one of the interior surface and the exterior surface, wherein the coating having a surface energy of not more than 50 mJ/m²; and

one of fluid pressure pulsation generating device and a vibration generating device,

wherein the fluid pressure pulsation generating device applying fluid pressure pulsations to the petroleum-based liquid,

wherein the vibration generating device applying mechanical vibration to housing and the plurality of tubes.

26. The heat exchanger according to claim 25, wherein the heat exchanger includes a fluid pressure pulsation generating device, wherein the device generating fluid pressure pulsations are generated at a frequency in the range of 0.1 Hz to 20 kHz.

27. The heat exchanger according to claim 25, wherein the adherent fouling resistant coating comprises:

a layer of organometallic molecules having a thickness of 1 to 10 molecular layers, wherein the layer will not undergo substantial decomposition at temperatures up to 450° C., and wherein the layer has a surface energy lower than 50 millijoule/m².

28. The heat exchanger according to claim 26, wherein the layer of organometallic molecules is deposited on 80 to 100% of the inner wall surface.

29. The heat exchanger according to claim 26, wherein the metal in the organometallic compound is silicon.

30. The heat exchanger according to claim 26, wherein the organo moiety in the organometallic compound is a hydrocarbyl group from 1 to 30 carbon atoms.

31. The heat exchanger according to claim 30, wherein the hydrocarbyl group is aliphatic or aromatic and is substituted with at least one functional group.

32. The heat exchanger according to claim 26, wherein the organometallic compound is an alkoxy silane, silane, silazone or phenyl siloxane.

33. The heat exchanger according to claim 26, wherein the organometallic compound is hexamethyldisiloxane.

34. The heat exchanger according to claim 25, wherein the surface energy of the coating is between 18 and 50 mJ/m².

35. The heat exchanger according to claim 25, wherein the coating has a surface with a water contact angle from 95° to 160°.

36. The heat exchanger according to claim 35, wherein the water contact angle is from 110° to 150°.

37. The heat exchanger according to claim 35, wherein the water contact angle is from 130° to 160°.

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