This invention relates to a method of chemically treating hydrocarbon liquids which contact surfaces under high temperature conditions in order to inhibit, prevent and/or reduce the deposition of substances thereon. More specifically, this invention relates to a chemical treatment of the metal surfaces in contact with petroleum hydrocarbon liquids under conditions of high temperatures whereby said liquids tend to form deposits on such metal surfaces. This invention also relates to compositions employed in these processes.

In the processing of hydrocarbon liquids, particularly petroleum hydrocarbon liquids, elevated temperatures are often used in many necessary and important operations. To handle liquids at elevated temperatures, heat exchangers and the like devices are often employed to control the heat transfer rate from one operational step to another. When hydrocarbon liquids contact hot metal surfaces, there is sometimes a tendency for the liquid to decompose or undergo a chemical reaction that manifests itself in the form of deposits. These deposits may be either coke-like or they may be in the form of tenacious, soft, sticky sludge which adheres to hot surfaces. Adherence of deposits, rather than the deposit formation itself, is the essence of the problem, in contrast to fuel storage where residue in the oil itself creates the problem.


These deposits tend to materially decrease the heat transfer capacities of the metal surfaces and hence increase operating expenses. These deposits also require additional effort and time to remove and to restore the equipment to its original operating efficiency.

Petroleum refinery operations often encounter the above described conditions in many stages in the refining process. These deposits form on heat transfer surfaces at temperatures as low as about 200-225°F, and may be evidenced at temperatures as extreme as 800°F.

It is practically impossible to prevent these deposits by coating the metal surfaces with a protective permanent coating due to the possible loss of heat transfer. In addition, the large volume of liquid that contacts such equipment increases the problem of treating metal surfaces in petroleum processing to prevent high temperature deposits.

It would be advantageous if a chemical agent could be added in an extremely small amount to a hydrocarbon liquid which tends to form high temperature deposits whereby such deposits would be prevented. It would also be desirable if such a chemical would not only prevent such deposits but would also remove them without necessitating the stoppage of a given operation. It therefore becomes an object of the present invention to prevent the formation of high temperature deposits on metal surfaces by chemical means.

Another object is to furnish a chemical which when added to a hydrocarbon liquid will prevent the deposit-forming tendencies of said liquid when it contacts metal surfaces at elevated temperatures.

A further object is to provide a chemical treatment which will prevent the formation of high temperature deposits by petroleum hydrocarbon liquids in contact with heat transfer equipment.

Yet another object is to furnish a chemical treatment capable of being combined with a thermally unstable, deposit-forming liquid whereby said liquid will not form deposits upon metal surfaces at elevated temperatures.

Still another object is to provide a chemical treatment which will remove high temperature deposits from metal surfaces of petroleum refining equipment without the necessity of stopping the operations of such equipment.

Other objects will appear hereinafter.

In accomplishing these objects in accordance with the invention it has been found that new and improved results in preventing, inhibiting and/or reducing the formation of deposits from petroleum hydrocarbon liquids during the processing thereof at elevated temperatures, particularly at temperatures within the range of about 200-225°F to 800°F, are obtained by adding to, preferably by dissolving or dispersing in the hydrocarbon liquid the anti-fouling agent of this invention.

In application Ser. No. 50,558, filed Aug. 19, 1960, I have described and claimed various compositions useful as anti-fouling agents.

These anti-fouling agents include a partial ester of a polyl and a carboxylic acid, said partial ester being soluble and/or dispersible in the hydrocarbon liquid, wherein at least one but not all of the hydroxy groups of the polyl are esterified with a carboxylic acid.

Although the partial ester can be employed alone, its activity is enhanced by one or more of the following oil soluble or dispersible auxiliary agents:

(1) An oxylation phenol.

(2) A copolymer of (a) an acrylic type ester and (b) vinyl pyrrolidene (sometimes referred to herein as “co-polymer”).

(3) A metal deactivator.

I have now discovered that the compositions described therein can be rendered more effective as anti-fouling agents. These compositions, particularly at temperatures above 500°F, by incorporating therein salts of an organic sulfonic acid which are at least oil dispersible or oil soluble.

The anti-fouling agents employed in S.N. 50,558 are described therein as follows:

The anti-fouling agent employed in this invention is a partial ester of a polyl and a carboxylic acid. Although partial esters formed from monocarboxylic acids are preferred, partial esters of polyls and polycarboxylic acids, particularly dicarboxylic acids, can be employed provided they are soluble or dispersible in hydrocarbon, for example a partial ester polymer of a diol and a dicarboxylic acid

\[
\text{HO-} \left( \text{O-B-O-G-O} \right)_{n} \text{-H}
\]

wherein B is the acid moiety (an alkylene, arylene, cycloalkylene, etc. radical) and G is the polyl moiety (an alkylene, oxyalkylene, poloxyalkylene, etc. radical). Another example of a suitable partial ester of a dicarboxylic acid and a diol is

\[
\text{HO-G-O-B-O-G-OH}
\]

Examples of polycarboxylic acids include the alkylene polycarboxylic acids, the arylene polycarboxylic acids,
3,328,283

the aralkylene polycarboxylic acids, etc. Specific examples of dicarboxylic acids include

\[
\text{HO}_2\text{C-}\text{B-}\text{C}-\text{OH}
\]

where B is alkylene, arylene, etc., for example, succinic, alkenyl succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, dimeric etc. acids. Examples of aromatic dicarboxylic acids include phthalic, isophthalic, terephthalic acid, biphenyl dicarboxylic acid, etc.

Examples of polyols include diols, triols, tetrals, pentols, hexols, etc. for example glycols, glycerol, polymerized glycerols, trimethyl ethane, sorbitol, mannitol, mannannide, mannitan, sorbide, sorbitan, pentaerythritol, etc.

Examples of glycols include the alkylene glycols, HO-alkylene-OH, for example where the alkylene group has 2-20 or more carbons but preferably 2-8 carbons, with an optimum of 2-4 carbons and polyoxyalkylene glycols, for example, the formula, HO(alkylene)O)nH where the alkylene group is, for example, ethylene, propylene, butylene, mixtures of blocks thereof, etc. and n is 1-100, for example 1-20, but preferably 1-10. Non-limiting examples include ethylene glycol, propylene glycol, diethylene glycol, diethylene glycol, triethylene glycol, tripropylene glycol, pentaethylene glycol, pentaethylene glycol, decamethylene glycol, hexadecamethylene glycol, hentaconethylene glycol, the "Pharnetics" of Wyandotte Chemical Company, etc.

A class of partial esters utilisable in this invention include esters of hexitans and hexides obtained by dehydrating sorbitol, and certain polyoxyalkylanes, such as the polyoxyethylene and derivatives thereof. These compounds are known as "Spans" and "Tweens", which are manufactured by the Atlas Powder Company. According to the manufacturer's literature, these esters are prepared by first dehydrating sorbitol to produce a mixture of hexitans and hexides having the following formula:

\[
\begin{align*}
\text{R} \cdot \text{CH} \cdot & \text{CH} \cdot \text{OH} \\
\text{HO} \cdot \text{CH} \cdot & \text{CH} \cdot \text{OH} \\
\text{CH} \cdot & \text{OH} \\
\text{OH} \\
\text{OH} \cdot & \text{CH} \cdot \text{CH} \cdot \text{OH} \\
\text{OH} \cdot & \text{OH} \\
\text{OH} \\
\end{align*}
\]

This mixture of hexitans and hexides is then esterified by reacting it with one or more moles of a fatty acid to form the "Spans." The "Tweens" are similar theroeto except that the unesterified hydroxy groups in the hexitans and hexides have polyoxyalkylene chain attached thereto. Non-limiting examples of the esters contemplated herein are sorbitol anhydride monolaurate, sorbitol anhydride monomyristate, sorbitol anhydride monopalmitate, sorbitol anhydride monostearate, sorbitol anhydride monoleate, sorbitol anhydride monolinoleate, and polyoxyethylene derivatives of the foregoing moesters. Further data on the moesters utilizable herein are attainable in a brochure entitled "Atlas Surface Active Agents" published in 1948 by the Atlas Powder Company. Reference should be made thereto, and it is considered to be a part of this specification.

I advantageously employ a compound of the formula

\[
\text{R'OH} \cdot \text{O-} \text{C-} \text{R''}
\]

where R is an alkylene radical derived from an alkylene oxide, for example ethylene oxide, propylene oxide, butyl-1,4-ene oxide, etc., and where R' is the radical derived from the carboxylic acid, for example, an aliphatic, a cycloaliphatic group, an aryl group, substituted groups thereof, etc., but preferably an alkyl group having sufficient carbons therein to make the product oil soluble or dispersible for example 6-20 or more carbons with an optimum of 10-20 carbons. In the preferred embodiment the polyol should have at least one unesterified hydroxyl group, for example in the case of glycerol, one or two of the hydroxyl groups thereon are esterified by the carboxylic acid. These compounds, having at least one unesterified hydroxyl group, will be referred to herein as partial esters and can be expressed generally as

\[
\text{H(O)O}_n\text{G-}-(\text{O-C-R})_y,
\]

where R is the radical derived from the carboxylic acid and G is the radical derived from the poly and x and y are each at least 1 and the sum of x+y equals the number of hydroxyl groups originally present in the polyol.

Although the partial esters alone prevent fouling, their efficiency is often enhanced by the presence of other auxiliary chemical components.

One of these auxiliary chemical components is an oxyalkylated phenol, preferably an oxyalkylated substituted phenol, such as an alkyl phenol, for example those of the formula

\[
\text{HO}_m\text{C}_n\text{OH}
\]

where R'' is a substituted group, for example, a hydrocarbon group, such as an aryl radical, an aliphatic radical, preferably alkyl, for example containing 1-30 or more carbon atoms, such as 4-20 carbons, but preferably 8-18 carbons (including substituted groups containing other elements besides carbon and hydrogen, such as alkoxy, etc.). A is an alkylene radical derived from an alkylene oxide such as ethylene, propylene, butylene, etc. oxides added singly, mixed, blocked, etc., x represents the number of moles of alkylene oxide for example 1 to 100 or more, such as 1-20, preferably 1-10 and m represents the number of substituted groups, for example 1-2.

An example of an oil-soluble or dispersible polyoxyalkylane ether of an alkyl phenol is prepared by alkylation with an olefin containing at least 6, and preferably 9 to 18, carbon atoms under conditions adapted to furnish an alkyl phenol reaction product containing an average of 1 to 2 alkyl groups per phenol molecule. The olefins employed for the alkylation of phenol may be straight-chain olefins, such as those produced in the Fischer-Tropsch synthesis; branched-chain olefins, such as those formed in the polymerization of propylene and butylene; or mixtures of branched- and straight-chain olefins which are recovered from a heavy cracked naphtha by selective adsorption with silica gel. Alcohols or alkyl chlorides with carbon chains of suitable length may also be employed as the alkylating agents. Preferably, mixtures of C6 to C12 branched-chain olefins produced by polymerizing propylene are thus employed. The resulting alkyl phenol product which may contain from 15 to 20% by weight of dialkyl phenols, is condensed with ethylene oxide, propylene oxide, butylene oxide, individually or in combination, or a corresponding glycol. Ethylene oxide is usually preferred. Particularly suitable alkyl phenol polyoxyalkylene ethers are alkyl phenyl polyoxyethylene ethers containing an average of 10-20 alkyl carbon atoms and 1 to 10 oxyethylene groups.
Another auxiliary chemical component is the copolymer derived from an acrylic ester of the formula:

\[
\begin{align*}
Z & \equiv \text{O} \quad \text{O} \quad Y \\
\text{Y} & \equiv \text{O} \quad \text{CH} \equiv \text{CH}_2
\end{align*}
\]

and N-vinyl-2-pyrrolidone, for example a copolymer containing the following units:

\[
\begin{align*}
\text{CH} & \equiv \text{CH} \\
\text{N} & \equiv \text{O} \\
\text{Z} & \equiv \text{O} \quad \text{CH} \equiv \text{CH}_2
\end{align*}
\]

having a molecular weight for example of at least 50,000, for example 50,000–500,000, or higher, but preferably 100,000–400,000 with an optimum of 300,000–400,000 of which vinyl pyrrolidone comprises at least 1% by weight of the copolymer, for example 1–30%, but preferably 3–15% with an optimum of 5–10%; where Y is hydrogen, a lower alkyl group such as methyl, ethyl, etc., Z is an hydrocarbon group having, for example, 1–30 carbon atoms, but preferably 8 to 18 carbon atoms.

These polymers are preferably acrylic or methacrylic polymers, or polymers derived from both in conjunction with vinyl pyrrolidone. The Z group on the polymer, which can be the same throughout or mixed, can be octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, octadecyl, etc. Lower alkyl groups can also be employed such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, etc., but they preferably are employed as co-polymers of the higher Z groups, for example a copolymer of dodecyl methacrylate and methyl acrylate, etc.

The acrylic ester units may be derived from one or more acrylic type monomers and may be fully acrylic or fully methacrylic or both acrylic and methacrylic. The polymer may be random, block, graft, etc.

Also, Z may also be an alkalyzed aromatic group such as butyl phenyl, amyl phenyl, etc., or a cycloaliphatic group such as cyclohexyl. Thus, non-limiting specific examples of suitable monomeric esters are: methyl acrylate, ethyl acrylate, propyl methacrylate, amyl acrylate, lauryl acrylate, cetyl acrylate, octadecyl acrylate, amyl methacrylate, lauryl methacrylate, cetyl methacrylate, octadecyl methacrylate, amylphenyl methacrylate, cyclohexyl methacrylate, etc., including the analogous acrylate or methacrylate esters. Copolymers of the above and other acrylic esters may be used, for example, a copolymer of methyl or ethyl acrylate and dodecyl methacrylate in conjunction with vinyl pyrrolidone. However, it should be understood that this description does not preclude the presence of small amounts of unesterified groups being present in the polymer, i.e. approximately 5% or less of where Z=H.

It should be understood, of course, that the above compounds are polymerized, the polymerization should not be carried to such an extent as to form polymers which are insoluble or non-dispersible in the petroleum hydrocarbon used. The polymerization may be carried out by methods known to the art, such as by heating mildly in the presence of a small amount of benzoyl peroxide, but the method of polymerization is not part of this invention. For examples of acryl-vinyl pyrrolidone copolymers see French Patent 1,163,033.

Another auxiliary chemical component is a metal deactivator for example those conveniently employed in deactivating copper, iron and other metals from hydrocarbon systems. Typical examples are those described in U.S. Patent 2,282,513. Of course, one skilled in the art is aware that many other metal deactivators are known and can be employed herein.

The compounds employed as metal deactivators are preferably of the type of Schiff's bases and may be represented by the formulae:

\[
\begin{align*}
& (1) \quad \text{A} \quad \equiv \text{CH} \equiv \text{N} \quad \equiv \text{R} \quad \equiv \text{N} \quad \equiv \text{CH} \equiv \text{B} \\
& \text{and preferably,} \\
& (2) \quad \text{HO} \equiv \text{A} \quad \equiv \text{CH} \equiv \text{N} \quad \equiv \text{R} \quad \equiv \text{N} \quad \equiv \text{CH} \equiv \text{B} \equiv \text{OH}
\end{align*}
\]

wherein A and B each represents an organic radical and preferably a hydrocarbon radical. In Formula 2 A and B each preferably represents an aromatic ring or an unsaturated heterocyclic ring in which the hydroxyl radical is attached directly to a ring carbon atom ortho to the —CH=N group. R represents an aliphatic radical having the two N atoms attached directly to different carbon atoms of the same open chain.

Typical examples of aldehydes and polyamines employed in preparing these Schiff bases includes the following:

**Aldehydes:**
- Benzaldehyde
- 2-methylbenzaldehyde
- 3-methylbenzaldehyde
- 4-methylbenzaldehyde
- 2-methoxybenzaldehyde
- 4-methoxybenzaldehyde
- n-Naphthaldehyde
- b-Naphthaldehyde
- Phenylbenzaldehyde
- Propionildehyde
- n-Butylaldehyde
- Heptaldehyde
- Aldol
- 2-hydroxybenzaldehyde
- 2-hydroxy-6-methylbenzaldehyde
- 2-hydroxy-3-methoxybenzaldehyde
- 2,4-dihydroxybenzaldehyde
- 2,6-dihydroxybenzaldehyde
- 2-hydroxyanaphthaldehyde-1
- 1-hydroxynaphthaldehyde-2
- Anthrol-2-aldehyde-1
- 2-hydroxyfluorene-aldehyde-1
- 4-hydroxydiphenyl-aldehyde-3
- 3-hydroxyphenanthrene-aldehyde-4
- 1,3-dihydroxy-2,4-diodhdehyde-benzene
- 2-hydroxy-5-chlorobenzaldehyde
- 2-hydroxy-3,5-dibromobenzaldehyde
- 2-hydroxy-3-nitrobenzaldehyde
- 2-hydroxy-3-cyanobenzaldehyde
- 2-hydroxy-3-carboxybenzaldehyde
- 4-hydroxyprypidine-aldehyde-3
- 4-hydroxyquinoline-aldehyde-3
- 7-hydroxyquinoline-aldehyde-8

**Polyamines:**
- Ethylenediamine
- 1,2-propylene-diamine
- 1,3-propylene-diamine
- 1,6-hexamethylenediamine
- 1,10-decamethylene-diamine
- Diethylaminetamine
- Triethylenetetraamine
- Pentaerythritetetraamine
- 1,2-diaminocyclohexane
- Di-(b-aminomethyl) ether
- Di-(b-aminomethyl) sulfide

The partial ester comprises of at least 5% of the anti-fouling composition such as 5 to 100%, for example,
10 to 80%, preferably 15 to 60% with an optimum of 30 to 40%.

Where other auxiliary chemical components are employed in conjunction with the partial ester, they are employed in the following percentages of the total composition.

Oxyalkylated phenol—0 to 95%, for example, 10 to 80%, preferably 30 to 70%, with an optimum of 40 to 60%.

The copolymer—0 to 35%, for example, 1 to 25%, preferably 5 to 15% with an optimum of 8 to 12%.

Metal deactivators—0 to 10%, for example, 0.001 to 8%, preferably 0.1 to 5% with an optimum of 0.3 to 2%.

Thus, the partial ester may be effectively employed alone or in conjunction with the oxyalkylated phenol, and/or the copolymer and/or the metal deactivator. However, it should be noted that the optimum amounts of each will vary with the fuel, the conditions employed, the temperatures, etc.

Where the additive includes (1) the partial ester, (2) the oxyalkylated phenol and (3) the copolymer, typical weight percentage compositions are as follows:

### A. Broad range:
- (1) 5 to 95
- (2) 75 to 4
- (3) 20 to 1

### B. Preferred range:
- (1) 15 to 80
- (2) 70 to 18
- (3) 15 to 2

### C. Optimum range:
- (1) 25 to 45
- (2) 61 to 47
- (3) 14 to 8

Where the metal deactivator is employed, it is 0.001 40.

### TABLE II—OXYALKYLATED PHENOLS

<table>
<thead>
<tr>
<th>Ex.</th>
<th>R</th>
<th>m</th>
<th>AO</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nonyl</td>
<td>1</td>
<td>E0</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Butyl</td>
<td>2</td>
<td>E0</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>Phenyl</td>
<td>1</td>
<td>E0</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>Dodecyl</td>
<td>1</td>
<td>E0</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>Octadecyl</td>
<td>2</td>
<td>E0</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>Nonyl</td>
<td>2</td>
<td>E0</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>Butyl</td>
<td>2</td>
<td>E0</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>Octadecyl</td>
<td>1</td>
<td>E0</td>
<td>25</td>
</tr>
<tr>
<td>9</td>
<td>Nonyl</td>
<td>2</td>
<td>E0</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>Butyl</td>
<td>2</td>
<td>E0</td>
<td>50</td>
</tr>
<tr>
<td>11</td>
<td>Octadecyl</td>
<td>1</td>
<td>E0</td>
<td>15</td>
</tr>
<tr>
<td>12</td>
<td>Dodecyl</td>
<td>1</td>
<td>E0</td>
<td>15</td>
</tr>
<tr>
<td>13</td>
<td>Ethoxy</td>
<td>1</td>
<td>E0</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>Octadecyl</td>
<td>1</td>
<td>E0</td>
<td>15</td>
</tr>
<tr>
<td>15</td>
<td>Cardiol</td>
<td>1</td>
<td>E0</td>
<td>20</td>
</tr>
<tr>
<td>16</td>
<td>Hydrogenated cardiol</td>
<td>1</td>
<td>E0</td>
<td>20</td>
</tr>
</tbody>
</table>

### TABLE III—VINYL PYRROLIDONE-ACRYLIC ESTER-TYPE RESINS

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Monomer 1</th>
<th>Monomer 2</th>
<th>Monomer 3</th>
<th>Vinyl Pyrrolidone, percent by wt.</th>
<th>Mol Ratio</th>
<th>Av. Mol Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tridecyl methacrylate</td>
<td>Octadecyl methacrylate</td>
<td></td>
<td>7.5</td>
<td>1:1</td>
<td>300,000</td>
</tr>
<tr>
<td>2</td>
<td>Dodecyl methacrylate</td>
<td>Butyl acrylate</td>
<td></td>
<td>10</td>
<td>2:1</td>
<td>400,000</td>
</tr>
<tr>
<td>3</td>
<td>Butyl acrylate</td>
<td></td>
<td></td>
<td>5</td>
<td>2:1</td>
<td>300,000</td>
</tr>
<tr>
<td>4</td>
<td>Tridecyl methacrylate</td>
<td>Methyl methacrylate</td>
<td></td>
<td>10</td>
<td>2:1</td>
<td>400,000</td>
</tr>
<tr>
<td>5</td>
<td>Octadecyl methacrylate</td>
<td>Butyl acrylate</td>
<td></td>
<td>10</td>
<td>2:1</td>
<td>300,000</td>
</tr>
<tr>
<td>6</td>
<td>Cetyl methacrylate</td>
<td>Octadecyl methacrylate</td>
<td></td>
<td>7.5</td>
<td>2:1</td>
<td>300,000</td>
</tr>
</tbody>
</table>

To 8%, preferably 0.1 to 5%, with an optimum of 0.5 to 2%, based on the above mixture.

The following compounds are satisfactorily employed as anti-foulants.

### TABLE I—PARTIAL ESTERS

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Polyol</th>
<th>Acid</th>
<th>Mol Ratio Polyol/ Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethylene glycol</td>
<td>Dodecanol</td>
<td>1:1</td>
</tr>
<tr>
<td>2</td>
<td>Diethylene glycol</td>
<td>Stearic</td>
<td>1:1</td>
</tr>
<tr>
<td>3</td>
<td>Propylene glycol</td>
<td>Lauric</td>
<td>1:1</td>
</tr>
<tr>
<td>4</td>
<td>Diethylene glycol</td>
<td>Adipic</td>
<td>2:1</td>
</tr>
<tr>
<td>5</td>
<td>HO[EO]H</td>
<td>Lauric</td>
<td>2:1</td>
</tr>
<tr>
<td>6</td>
<td>HO[EO]H</td>
<td>Phtalate</td>
<td>1:1</td>
</tr>
<tr>
<td>7</td>
<td>HO[EO]H</td>
<td>Octanoic</td>
<td>1:1</td>
</tr>
<tr>
<td>8</td>
<td>Glycol</td>
<td>Lauric</td>
<td>2:1</td>
</tr>
<tr>
<td>9</td>
<td>HO[EO]H</td>
<td>Trimethylol</td>
<td>1:1</td>
</tr>
<tr>
<td>10</td>
<td>Tricresyl phosphate</td>
<td>Hexanoic</td>
<td>1:1</td>
</tr>
<tr>
<td>11</td>
<td>Ferric chloride</td>
<td>Lauric</td>
<td>1:2</td>
</tr>
<tr>
<td>12</td>
<td>Sorbitol</td>
<td>Palmitate</td>
<td>1:3</td>
</tr>
<tr>
<td>13</td>
<td>Mannitol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[B. Cyclic type]

$$[R(CO)\_2(\text{CH}_2\_\text{CHO})\_n\_H]$$

$$Z=\text{furan, pyran or condensed furan ring}$$

<table>
<thead>
<tr>
<th>Ex.</th>
<th>n</th>
<th>z</th>
<th>x</th>
<th>O</th>
<th>RC=</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>Lauryl</td>
<td>Tween 21.</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>Stearyl</td>
<td>Tween 61.</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>Oleyl</td>
<td>Tween 81.</td>
</tr>
<tr>
<td>19</td>
<td>3</td>
<td>10</td>
<td>2</td>
<td>Lauryl</td>
<td>Tween 83.</td>
</tr>
<tr>
<td>20</td>
<td>3</td>
<td>10</td>
<td>2</td>
<td>Stearyl</td>
<td>Tween 60.</td>
</tr>
<tr>
<td>21</td>
<td>1</td>
<td>3</td>
<td>10</td>
<td>Lauryl</td>
<td>Tween 83.</td>
</tr>
<tr>
<td>22</td>
<td>1</td>
<td>3</td>
<td>10</td>
<td>Stearyl</td>
<td>Tween 83.</td>
</tr>
<tr>
<td>23</td>
<td>1</td>
<td>3</td>
<td>10</td>
<td>Oleyl</td>
<td>Tween 60.</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>3</td>
<td>10</td>
<td>Lauryl</td>
<td>Span 20.</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>3</td>
<td>10</td>
<td>Stearyl</td>
<td>Span 40.</td>
</tr>
<tr>
<td>26</td>
<td>1</td>
<td>3</td>
<td>10</td>
<td>Oleyl</td>
<td>Span 60.</td>
</tr>
</tbody>
</table>
The specification of S.N. 50,558 is hereby incorporated by reference into the present application. The compositions described in S.N. 50,558 can be rendered more effective by incorporating therein salts of organic sulfonates. This is particularly true when the temperatures employed are above 50° F., such as 350°-680° F. or higher.

The organic sulfonate salts may be represented by the following formula, \((\text{RSO}_3)\_\text{Me}\), examples of which are petroleum sulfonate salts, alkyl aryl sulfonate salts, for example those of the formula \(\text{R}_n-\text{Ar}-\text{SO}_3\text{Me}\), where \(\text{Me}\) represents a salt forming moiety, for example the elements of Group I-A, Group II-A, etc. of the periodic table, ammonium and amine salts thereof, etc. \(\text{Ar}\) represents an aromatic group, for example, phenyl, naphthyl, higher condensed aromatic systems, and \(\text{R}\) represents a substituted group, for example, a hydrogen-carbon group such as alkyl, \(x\) is an integer determined by the valence of the metal, and \(n\) represents the number of positions on the aromatic nucleus which are substituted. Further examples of alkyl aryl sulfonates are presented in the following table:

**TABLE IV.—ALKYL AROMATIC SULFONATES**

<table>
<thead>
<tr>
<th>Alkyl group</th>
<th>Aromatic nucleus</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Benzene</td>
<td></td>
</tr>
<tr>
<td>B. Toluene</td>
<td></td>
</tr>
<tr>
<td>C. Xylenes, ethyl benzene, mesitylene, cyanene, etc.</td>
<td></td>
</tr>
<tr>
<td>D. Phenol</td>
<td></td>
</tr>
<tr>
<td>E. Cresols, xylenols, and lower alkylated phenols</td>
<td></td>
</tr>
<tr>
<td>F. Phenol ethers, anisole, phenetole, etc.</td>
<td></td>
</tr>
<tr>
<td>G. Diaryl ethers, diphenyl ether, etc.</td>
<td></td>
</tr>
<tr>
<td>H. Naphthalene</td>
<td></td>
</tr>
<tr>
<td>I. Naphthols</td>
<td></td>
</tr>
<tr>
<td>J. Naphthol ethers</td>
<td></td>
</tr>
<tr>
<td>K. Diphenyl</td>
<td></td>
</tr>
<tr>
<td>L. Phenyl phenols</td>
<td></td>
</tr>
<tr>
<td>M. Di- and triphenyl methanes</td>
<td></td>
</tr>
<tr>
<td>N. Benzoids and desoxybenzoids</td>
<td></td>
</tr>
<tr>
<td>O. Rosin and modified rosins</td>
<td></td>
</tr>
</tbody>
</table>

The compositions of S.N. 50,558 can be improved by adding thereto sufficient sulfonate to improve the anti-fouling properties thereof, for example at least 5% by weight organic sulfonate, such as 5 to 95%, for example 20 to 80%, but preferably 30 to 70% with an optimum of 40 to 60%. Of course, the amount of effective sulfonate will depend, among other things, on the specific sulfonate employed, the hydrocarbon treated, etc.

The conditions encountered in refinery operations are simulated by exposing petroleum products taken from various refinery distillate high temperature heat exchange tubes in the absence of and in the presence of the anti-fouling compositions of this invention. A CFR fuel coker model 01FC is employed to simulate these conditions. It is described in CRC Manual No. 3, March 1957, published by the Coordinating Fuel and Equipment Research Committee of the Coordinating Research Council, Inc. The standard procedure is employed except that the equipment is modified so as to bypass the filter section.

The conditions of the test are as follows:

- **Test time** 60 min
- **Test temperature** 140° F.
- **Test pressure** 250 lbs./hr.
- **Test rate of flow** 3 lbs./hr.

The amount of fouling occurring is measured by observing the preheater (or heat exchanger) tube before and after the test to determine the amount of deposits formed on the preheater tube. One finds the tube appearance to correspond with the amount of fouling measured by gravimetric means, for example, a tube showing 2.0 mg. deposit will look considerably cleaner than one showing 4.0 mg. deposit. Gravimetric results generally corroborate the results obtained by inspection of the tube. The following tests were run on a straight run naphtha charge. In the following tests, the additive is designated as follows:

**F. (Composition of S.N. 50,558):**

- Parts by weight
  - 50% Dinitrol phenol-
  - 10% M ElO
  - 5% Lauric acid ester of diethylene glycol
  - 3.5% Terpolymer of lauryl methacrylate cetyl-stearyl methacrylate, and vinyl pyrrolidone

A. Blend of alkyl aryl polyether alcohol:

![alkyl polyether alcohol](image)

C. Mixture of 1 part, by weight, barium petroleum Sulfonate, 2.5 parts calcium Sulfonate and 1.5 parts sodium sulfonate.

M. Calcium petroleum sulfonate: Mol. wt. 900.
All of the organic sulfonates employed in the above table are oil soluble and can be described by the formula

$$[\text{C}_8\text{H}_{12n-18}]\text{SO}_4\text{Me}$$

where Me is a metal of valence $x$, and $n$ is greater than 20.

The above tests are typical of the screening tests employed in evaluating anti-fouling additives. After being screened in this manner, the anti-fouling additives are employed in petroleum refinery operations. By means of the above tests, the most effective additive is selected for the particular hydrocarbon under consideration and the additive is then employed in the specific operation.

The anti-fouling additive can be employed in refining crude petroleum as well as in the treatment of any component thereof which are exposed to high temperatures including the light distillates, for example light naphthas, intermediate naphthas, heavy naphthas, etc.; middle distillates, for example kerosene, gas oil, etc; distillate lube oil stocks, for example, white oil, saturating oil, light lube oil, medium lube oil, heavy lube oil, and the like.

In addition, the additive can be employed with other hydrocarbons such as xylene, benzene, purified hydrocarbon compounds, etc. In addition, they can be employed under certain conditions with non-hydrocarbons, such as alcohols, phenols, etc. For example, they can be employed in a toluene extraction tower and stripper which process comprises mixing phenol and toluene in an extraction whereby phenol extracts impurities from toluene and the raffinate is subsequently removed. Thereafter the mixture is sent to a stripper where the toluene is removed from the phenol by distillation. The remaining phenol is recycled to the extractor for further use. The system is operated over a wide temperature range for example 230–425° F. Deposits in the phenol circuit cause the loss of excessive amounts of phenol. It can be used in heat transfer units used in a furfural extraction process processing for example, intermediate distillates, paraffin distillates, decanted oil, vacuum cylinder stock, desphalted cylinder stock, etc.

The amount of anti-fouling agent required in this invention is subject to wide variation but in general very effective results have been obtained by adding relatively minute amounts of the anti-fouling agent to the hydrocarbon being processed, for example, amounts may be as low as 0.5 p.p.m. in hydrocarbon liquid, for example 1 to 500 p.p.m. or higher, for example 1000 or more p.p.m., preferably 25 to 100 p.p.m., with an optimum of 35–55 p.p.m. Higher temperature requires greater concentration.

In general, the upper limit is determined by the economics of the process but other factors should be taken into consideration such as whether large amounts will have any adverse effects on present or subsequent operations. Because of the many different types of operations where hydrocarbons are heated to elevated temperatures under conditions where deposits are formed, it is difficult to give specific ranges which will be effective in all operations. The amount of agent which inhibits the formation of deposits is referred to herein as an “anti-fouling amount.”

The above figures relate to p.p.m. in terms of active anti-fouling chemical not including the solvent employed.

Inasmuch as the anti-fouling agent is employed in such small amounts and it is preferable to feed them continuously or semi-continuously by means of a proportioning pump or other suitable device to the particular hydrocarbon liquid being processed or to add them in a similar manner to the apparatus in which the hydrocarbon liquid is being processed, it is desirable to incorporate the agent or a mixture of agents into a suitable solvent which will be compatible with the liquid which is to be processed. The solvent which is used to dissolve the active ingredient is also subject to some variation depending upon the solubility characteristics of the particular compound employed. In some cases, even though the active mixture is insoluble in a particular solvent, it will dissolve in a combination of solvents.

In the practice of the invention it is very desirable to start the treatment with the chemicals employed for the purpose of the invention at a higher dosage and then gradually reduce the dosage to the point where fouling of the apparatus is just eliminated.

The invention is especially valuable where sour naphthas are being processed or where the oil being processed is a mixture containing some sour naphthas.

Examples of specific types of apparatus to which the chemical compositions of the invention can be added during petroleum processing are fractionating towers, stripping columns, debenzonizers, dephosphonizers, desulfonizers, heat exchangers, reboilers, hot product lines and other metal equipment (usually ferrous metal) which is brought into contact with the organic liquids being processed at relatively high temperatures. The invention makes it possible to extend the useful life of crude oil fractionating towers and other types of petroleum equipment. It also makes it possible to provide cleaner inside surfaces resulting in better fractionating, better heat exchange in coolers, far less severe plugging and less time required for cleaning and maintenance.

Having thus described my invention what I claim as new and desirable to obtain by Letters Patent is:

1. A process for inhibiting in oil refining apparatus during petroleum refining operations the formation of adherent coke-like deposits and adherent tenacious soft, sticky sludges on, and the adhesion of said deposits and said sludges to, the hot metal heat transfer surfaces of a heat exchanger in said oil refining apparatus by a hydrocarbon liquid passing through said heat exchanger at a temperature in excess of about 225° F. and having the tendency to undergo a chemical reaction at a temperature in the range of about 225° F. to about 800° F., said chemical reaction manifesting itself in the form of adherent coke-like deposits and adherent soft, sticky sludges, such as are usually formed during passage of said hydrocarbon liquid through said heat exchanger and in contact with the hot metal surfaces of said heat exchanger in said oil refining apparatus at a temperature in the range of about 225° F. to about 800° F. characterized by

(1) Incorporating in said hydrocarbon liquid prior to contact with said hot metal surfaces of said heat exchanger in said oil refining apparatus an antifouling amount of a composition comprising

(A) a partial ester selected from the group consisting of

$$\text{(HOR)}_2-G-(O-C-R)_{n-1}$$

where:

- $G$ is the hydrocarbon-containing moiety of a polyol,
- $x$ is an integer of at least 1,
3,328,283

y is an integer of at least 1, the sum of x and y being equal to the number of hydroxyl groups originally present in the polyol, and

R is a hydrocarbon radical having 6–20 carbon atoms selected from the group consisting of an aryl radical and an aliphatic radical

(2) a partial ester of a polyol and a polycarboxylic acid,

(3) partial esters formed by first dehydrating sorbitol to produce a mixture of hexitons and hexides having the formula

![Chemical Structure]

and then esterifying said mixture by reacting it with at least one mole of a fatty acid selected from the group consisting of lauric acid, stearic acid, palmitic acid and oleic acid, and

(4) partial esters formed by first dehydrating sorbitol to produce a mixture of hexitons and hexides having the formula

![Chemical Structure]

then esterifying said mixture by reacting it with at least one mole of a fatty acid selected from the group consisting of lauric acid, stearic acid, palmitic acid and oleic acid, and then adding polyoxymethylene chains to the nonesterified hydroxy groups in said hexitons and hexides, and

(B) a hydrocarbon soluble salt selected from the group consisting of

(1) a petroleum sulfonate salt having the general formula

\[ \text{Me} \text{(CH}_2\text{H}_n\text{CH}_2\text{O})_{x}\text{X} \text{Me} \]

wherein:

Me is a metal of valence x, x is an integer of 1–2, and
\( n \) is an integer greater than 20,

(2) mixtures of petroleum sulfonate salts, each having the general formula of said salt of (1) and Me of each being different, and

(3) an alkyl aryl sulfonate salt having the formula

\[ (R_0\text{—Ar—SO}_3\text{)Me} \]
(1) partial esters formed by first dehydrating sorbitol to produce a mixture of hexitans and hexides having the formula

\[
\begin{align*}
\text{CH}_2 - \text{CH} - \text{CH} - & \text{OH} \\
\text{HO} - \text{CH} - & \text{CH} - \text{OH} \\
\text{HO} - \text{CH} - & \text{CH} - \text{OH} \\
\text{CH} - & \text{CH} - \text{CH}_3 \\
\text{OH} & \text{OH} \\
\end{align*}
\]

and then esterifying said mixture by reacting it with at least one mole of a fatty acid selected from the group consisting of lauric acid, stearic acid, palmitic acid and oleic acid, and

(4) partial esters formed by first dehydrating sorbitol to produce a mixture of hexitans and hexides having the formula

\[
\begin{align*}
\text{CH}_2 - & \text{CH} - \text{CH}_3 \\
\text{HO} - \text{CH} - & \text{CH} - \text{OH} \\
\text{HO} - \text{CH} - & \text{CH} - \text{OH} \\
\text{CH} - & \text{CH} - \text{CH}_3 \\
\text{OH} & \text{OH} \\
\end{align*}
\]

then esterifying said mixture by reacting it with at least one mole of a fatty acid selected from the group consisting of lauric acid, stearic acid, palmitic acid and oleic acid, and then adding polyoxyethylene chains to the nonesterified hydroxy groups in said hexitans and hexides, and

(B) a hydrocarbon soluble salt selected from the group consisting of

(1) a petroleum sulfonate salt having the general formula

\[
\text{Me} - \text{C}_{12-18} - \text{SO}_3 \text{Na}
\]

wherein:

- \text{Me} is a metal of valence \(x\),
- \(x\) is an integer of 1–2, and
- \(n\) is an integer greater than 20,

(2) mixtures of petroleum sulfonate salts, each having the general formula of said salt of (1) and \(n\) of each being different, and

(3) an alkyl aryl sulfonate salt having the formula

\[
(\text{Ar}-\text{SO}_3 \text{Me})
\]

wherein:

- \(\text{Me}\) is a metal of valence \(z\),
- \(z\) is an integer of 1–2,
- \(\text{Ar}\) is an aromatic radical,
- \(R\) is a hydrocarbon-containing radical having 1–18 carbon atoms, and
- \(x\) is an integer of 1–3, representing the number of nuclear substituted groups on said aromatic radical, and

(C) a member selected from the group consisting of

(1) an oxyalkylated hydrocarbon-substituted phenol having the formula

\[
\begin{align*}
\text{O} \quad \text{OH} \\
\text{O} \quad \text{OH} \\
\text{O} \quad \text{OH} \\
\end{align*}
\]

where:

- \(A\) is an alkylene radical having 2–4 carbon atoms,
- \(m\) is an integer of 1–2,
- \(x\) is an integer of 1–2, and
- \(R''\) is a hydrocarbon-containing radical having 1–30 carbon atoms selected from the group consisting of an alkyl radical, an aryl radical, and an aliphatic hydrocarbon radical,

(2) a copolymer containing the units

\[
\begin{align*}
\text{CH} - & \text{CH} \\
\text{CH} - & \text{CH} \\
\end{align*}
\]

and having a molecular weight of 50,000–500,000, unit (b) being at least 1–30% by weight of the copolymer, \(Y\) being selected from the group consisting of hydrogen and a lower alkyl group and \(Z\) being a hydrocarbon radical having 1–30 carbon atoms, and

(3) a Schiff base alkylene polyamine-aldehyde reaction product, and

(2) heating said hydrocarbon liquid having incorporated therein said composition in an antifouling amount to a temperature in the range of about 225° F. to about 800° F. by contact with said hot metal surfaces of said heat exchanger in said oil refining apparatus.

6. The process of claim 5 wherein the partial ester is of the formula

\[
\text{H}(\text{O alkylene})_2 \text{O} - \text{R}'
\]

wherein:

- \(n\) is an integer of 1–10, and
- \(R'\) is a hydrocarbon radical containing 6–20 carbon atoms.

7. The process of claim 5 wherein the partial ester is of the formula

\[
\text{R} = \text{SO}_3 \text{Me}
\]

wherein:

- \(\text{R}\) is an alkylene radical having 2–4 carbon atoms and
- \(\text{R}'\) is an alkyl group having 6–20 carbon atoms.

8. A process for inhibiting in oil refining apparatus during petroleum refining operations the formation of adherent coke-like deposits and adherent tenacious soft, sticky sludges on, and the adhesion of said deposits and said sludges to, the hot metal heat transfer surfaces of a heat exchanger in said oil refining apparatus by a hydrocarbon liquid passing through said heat exchanger at a temperature in excess of about 225° F. and having the tendency to undergo a chemical reaction at a temperature in the range of about 225° F. to about 800° F., said chemical reaction manifesting itself in the form of adherent coke-like deposits and adherent soft, sticky sludges, such as are usually formed during passage of said hydrocarbon liquid through said heat exchanger and in contact with the hot metal surfaces of said heat exchanger in said oil refining apparatus at a temperature in the range of about 225° F. to about 800° F. characterized by
(1) incorporating in said hydrocarbon liquid prior to contact with said hot metal surfaces of said heat exchanger in said oil refining apparatus an anti-fouling amount of a composition comprising

(A) a partial ester having the formula

\[ \text{H(OCH}_2\text{CH}_2\text{OH)}_n\text{O} - \text{C}_6\text{H}_5 \]

and

(B) a hydrocarbon soluble salt selected from the group consisting of

(1) a petroleum sulfonate salt having the general formula

\[ [\text{C}_9\text{H}_{2n-16}\text{SO}_4]_x\text{Me} \]

wherein:

- Me is a metal of valence \( x \),
- \( x \) is an integer of 1–2,
- \( n \) is an integer greater than 20,
(2) mixtures of petroleum sulfonate salts, each having the general formula of said salt of (1) and Me of each being different, and
(3) an alkyl aryl sulfonate salt having the formula

\[ (\text{R}_x - \text{Ar} - \text{SO}_4)_2\text{Me} \]

wherein:

- Me is a metal of valence \( z \),
- \( z \) is an integer of 1–2,
- Ar is an aromatic radical,
- \( R \) is a hydrocarbon-containing radical having 1–18 carbon atoms, and
- \( x \) is an integer of 1–3, representing the number of nuclear substituted groups on said aromatic radical, and

(C) a member selected from the group consisting of

(1) a copolymer of stearyl methacrylate and vinyl pyrrolidone and

(2) heating said hydrocarbon liquid having incorporated therein said composition in an antifouling amount to a temperature in the range of about 225°F. to about 800°F. by contact with said hot metal surfaces of said heat exchanger in said oil refining apparatus.

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DELBERT E. GANTZ, Primary Examiner.

PAUL M. COUGHLAN, Examiner.

A. RIMENS, Assistant Examiner.