United States Patent Office

3,437,583

Patented Apr. 8, 1969

3,437,583

ANTI-FOULANT AGENTS FOR PETROLEUM HYDROCARBONS

Gerardo A. Gonzalez, Philadelphia, Pa., assignor to Betz Laboratories, Inc., Trevose, Pa., a corporation of Pennsylvania

No Drawing. Continuation-in-part of application Ser. No. 595,045, Nov. 17, 1966. This application June 13, 1967, Ser. No. 645,590

Int. Cl. C23f *11/00;* **C09k** *3/00;* **C10g** *9/16*

U.S. Cl. 208—48 **15 Claims**

ABSTRACT OF THE DISCLOSURE

Anti-foulants for petroleum hydrocarbon streams and feedstocks which employ the combination of a metal deactivator, a phenolic compound and substituted succinic acids or anhydrides.

The present invention is a continuation-in-part of copending U.S. application Ser. No. 595,045 which was filed on Nov. 17, 1966.

In the processing of petroleum hydrocarbons and feedstocks such as petroleum process intermediates, petrochemicals and petrochemical intermediates, e.g., gas oils and reformer stocks, the hydrocarbons are commonly heated to temperatures in excess of 250° F. Similarly, such petroleum compounds are frequently subjected to heat exchange during processing and are often used as the heating medium on the "hot side" of heating and heat exchange systems. During such processing the petroleum hydrocarbons experience elevated temperatures which produce a separate phase commonly referred to as fouling deposits, within the petroleum compound. Such deposits are highly undesirable in that they reduce the bore or capacity of conduits and vessels to impede process throughput, impair thermal transfer, and clog filter screens, valves and traps. In the case of heat exchange systems, the deposits form an insulating layer upon the heat exchange surface to impair heat transfer and necessitate frequent shutdowns for cleaning, extended processing cycles, and increased coolant flow.

While the nature of such fouling deposits defies precise analysis, they appear to contain both carbonaceous phases of a coke-like nature, and polymers or condensates formed from the petroleum compound or impurities entrained therein. These condensates appear to interadhere the carbonaceous phase and to facilitate its adhesion to available surfaces. The catalysis of the formation of these polymers or condensates has been attributed to metal compounds such as copper or iron which are present in the petroleum compounds as impurities, or derived from the metallic receptacles in which the petroleum compounds are processed. For example, such metals may accelerate the hydrocarbon oxidation rate by promoting degenerative chain branching, while the resultant free radicals initiate oxidation and polymerization reactions which form gums and sediments.

In previous attempts to combat the formation of fouling deposits, it has been found that improvements may be realized by preventing the actual formation of these deposits, or preventing the adhesion of the deposits to available surfaces when formed. In addition, when heat transfer is the primary consideration in respect to such deposits, it has been found that desirable effects may be realized by influencing the density, and consequently the thermal insulating effect, of any deposits which may form and adhere to the heat transfer surfaces.

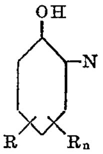
Previous attempts to control fouling deposits have employed phenolic compounds, e.g., U.S. 3,132,085 to Summers. Succinic derivatives have also been employed for this purpose, e.g., U.S. 3,271,295 and U.S. 3,271,296.

In the inventor's co-pending application Ser. No. 595,045, which was filed on Nov. 17, 1966, it was found that the combination of certain disclosed phenolic compounds and metal deactivators yield synergistic results as anti-fouling agents in petroleum compounds which are subjected to high temperatures. The present invention is based upon the discovery that a further synergistic improvement is realized when certain succinic derivatives are employed with the phenolic-metal deactivator compound.

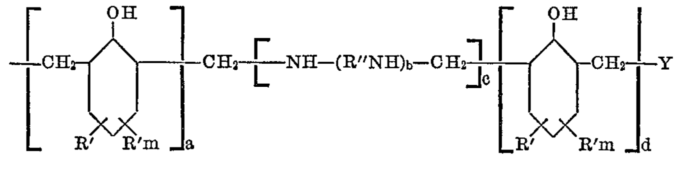
The ingredients of the anti-fouling agents of the present invention may be characterized as follows:

PHENOLIC COMPOUNDS

The phenolic compounds utilized in the practice of the invention are mono- and dialkyl substituted phenols, and the condensates of such phenols, including nitrogen containing phenolic condensates. These phenolic compounds and condensates may be represented by the formula:



in which R is an alkyl group attached to a carbon atom of the aromatic ring and contains between 4 to 12 carbon atoms, *n* is an integer having a value of between zero to 1, and X is a substituent selected from the group consisting of hydrogen and a phenolic condensate having the formula:



in which R′ is an alkyl group attached to a carbon atom of the aromatic ring and contains between 4 to 12 carbon atoms, R″ is a divalent hydrocarbon radical containing between 1 to 4 carbon atoms, Y is selected from the group consisting of hydroxyl and alkyl phenol, *a* and *d* are integers having a value of between zero to 15, *m* and *c* are integers having a value of between zero to one, *b* is an integer having a value of between zero to 4, and the sum total of *a* and *d* is no more than 25. It should be noted that when an excess of phenol is employed in the preparation of these condensates, Y will be the alkyl phenol which is employed in the condensation reaction. In other cases, methylol termination will be experienced and Y will be —OH.

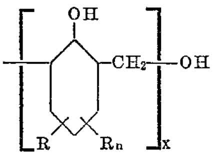
It should be noted that the alkyl substituents R and R′ are probably the primary factor contributing to the hydrocarbon solubility or dispersibility of these phenolic compounds and condensates. This solubility, when enhanced by the synergistic activity which is realized when the phenolic compounds are combined with the metal deactivator, yields the highly improved results which are realized with the invention.

While the nitrogen substituted alkyl phenol condensates are preferred ingredients of the inventive composition, highly satisfactory, and synergistically enhanced compositions have also been prepared from both the noncondensed alkyl phenols, and alkyl phenolic condensates which do not contain a nitrogen substituent.

Suitable alkyl phenols include butyl, octyl, nonyl, dioctyl and dinonyl phenol, although octyl phenol is a preferred material in respect to either the condensed or noncondensed compositions. In addition it appears that branched alkyl substituents, e.g. t-octyl, t-butyl, etc., enhance the hydrocarbon solubility or dispersibility of the inventive compounds and are preferred on that basis.

The suitable alkyl phenol condensates include both unsubstituted and nitrogen substituted condensates. The unsubstituted condensates are prepared by conventional means, employing either acidic or basic catalysts, to yield reaction products of the following type:

(I)



in which x is an integer having a value of between 1 to 25. While a 1:1 molar ratio of alkyl phenol:formaldehyde is preferred, a quantity of either reactant in excess of theoretical is acceptable. It should also be noted that when an excess of the alkyl phenol is employed, the uncondensed excess serves not only as a highly satisfactory diluent, but also contributes to the desired anti-fouling effect, since the prescribed alkyl phenols function as hydrocarbon dispersible anti-foulants in an uncondensed form and are synergized in the presence of the metal deactivator.

The nitrogen substituted reaction products may be prepared by condensing the alkyl or dialkyl phenol with either an ammonium compound, e.g., ammonium hydroxide, or an amine, e.g. ethylene diamine, propylene diamine, 1,3 diamino propane, etc. However, it should be noted that when the alkyl phenol is condensed with an ammonium compound such as ammonium hydroxide, the reaction conditions which are employed may determine whether the ammonium compound constitutes a nitrogen substituent to the resulting condensate, or merely catalyzes a reaction yielding a condensate such as that shown by Formula I above. Specifically, it has been found that high reaction temperatures, e.g. in excess of 150° C., may result in the temporary introduction of nitrogen within the condensate structure, but that the heat will eventually evolve the nitrogen to yield an unsubstituted condensate. However, a nitrogen determination, e.g. Kjeldahl, will permit the adjustment of the reaction conditions to yield the desired condensate, i.e. substituted or unsubstituted by nitrogen.

In the formation of all of the phenolic condensates of the invention, formaldehyde is employed as the coreactant with the alkyl phenol regardless of whether a nitrogen donating third reactant, i.e. amine or ammonium compound, is utilized.

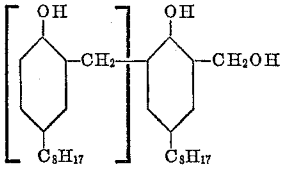
In the condensation reactions employing ammonium hydroxide for the preparation of nitrogen substituted condensates, a phenol:formaldehyde:ammonium hydroxide molar ratio of 1.5:1:2 is preferred. The excess ammonium compensates for losses due to violatility which may be further reduced through the use of a closed reaction system, whereas the excess of unreacted phenol serves as a satisfactory diluent, and as previously noted, even the uncondensed alkyl phenol is capable of contributing to the synergistic effect of the invention. While an excess of formaldehyde does not yield a beneficial effect, it does not appreciably impair the efficacy of the invention. When the ammonium compound is employed to merely catalyze, and not enter into the reaction, e.g. in a high temperature reaction, a substantial excess or this compound may be employed.

In the preparation of nitrogen substituted condensates from amines, a phenol:formaldehyde:amine molar ratio of 4:4:1 is preferred. Such as a ratio yields a desirable frequency of the nitrogen substituents, while an amine deficiency yields results similar to those obtained with the previously discussed condensates Formula I which are devoid of a nitrogen substituent. Similarly, a higher amine content, either as an unreacted excess, or as a more frequently occurring substituent, does not impair the efficacy of the invention.

Descriptions of the preparation of several phenolic compounds which have proved suitable for the practice of the invention, are provided by the following examples:

EXAMPLE 1

Octyl phenol, formaldehyde and ammonium hydroxide were employed in a 1.5:1:2 ratio. The octyl phenol and ammonium hydroxide were admixed, and an aqueous solution of formaldehyde (37% by weight of formaldehyde) was added thereto and further admixed. This reaction admixture was maintained at 170° F. for a period of 4 hours and then gradually elevated to a temperature of 360° F. during an additional 3 hour period. The reactants were maintained at 360° F. for an additional 20 minute period, during which time water was removed by distillation. The reaction product was then cooled to room temperature and admixed with an equal quantity of xylene. A Kjeldahl determination indicated that less than 1% nitrogen was present in the reaction product, and the molecular weight (A.H.T. Molecular Weight Apparatus determination) indicated a condensate of the following average structure:



The existence of this structure was further supported by infra-red and ultra-violet analyses, and solubility and fusability tests. The reaction product was also found to contain 12% by weight of unreacted octyl phenol.

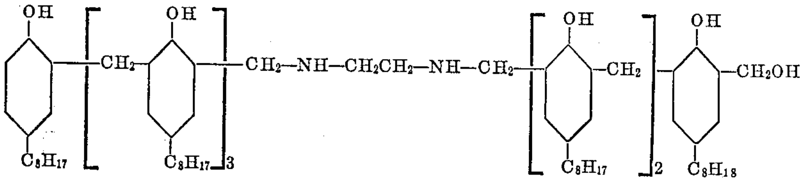
EXAMPLE 2

The reaction of Example 1 was repeated with a 0.6:1:0.8 ratio of octyl phenol:formaldehyde:ammonium hydroxide, with the reaction temperature reduced to 280° F. A Kjeldahl determination of the resulting condensate revealed 3.6% nitrogen which would indicate the presence of an ammonium molecule for each 1.7 mols of octyl phenol and 1.7 mols of formaldehyde.

Examples 1 and 2 have been employed to demonstrate that ammonium hydroxide may serve merely as a condensation catalyst, or may directly participate in the reaction to become a constituent of the reaction product.

EXAMPLE 3

Octyl phenol, formaldehyde and ethylene diamine were reacted in a 4:4:1 ratio by the method of Example 1. The formaldehyde employed was a 90% solution of paraformaldehyde. The reaction product was admixed with 60% by weight of a kerosene:xylene blend (1:3). Analysis revealed the presence of 2% of unreacted phenol while further study indicated a condensate having the average structure:



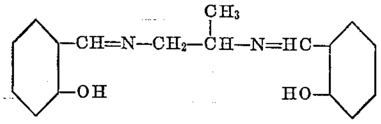
EXAMPLE 4

An admixture of 4 parts by weight of octyl phenol and 1 part of formaldehyde were reacted in the presence of 0.2% by weight of 90% formic acid.

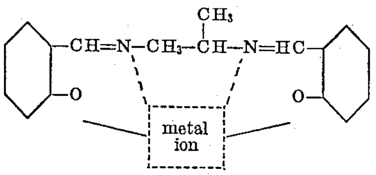
METAL DEACTIVATOR

More precisely, the present invention employs the combination of a metal deactivator and a phenolic compound. The inventive combination of ingredients provides a synergistic effect in that the cooperative action of the two ingredients is such that the total effect of the combination is greater than the sum of the effects of the two ingredients taken separately. As a consequence of the described synergism, the total quantity of anti-foulant employed may be reduced with appreciable reductions in the cost of the treatment, and less possibility of the formation of ancillary deposits from the anti-foulant. This reduction in the quantity of anti-foulant required, represents a substantial improvement over the anti-foulant agents of the prior art.

The metal deactivator employed in the practice of the present invention is N,N′-disalicylidene-1,2-propanediamine, havving the formula:



The coordinating effect of this compound upon the metals, e.g., copper and iron, which are believed to catalytically promote the formation of sludge in petroleum hydrocarbons during exposure to high temperatures, may be depicted as follows:

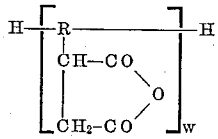


SUCCINIC DERIVATIVES

The succinic derivatives employed in the practice of the invention are reaction products of polyamines and substituted succinic acids or substituted succinic anhydrides.

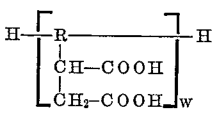
The substituted succinic acids and anhydrides utilized are represented by the formulae:

A)



and

(B)



$$H-\left[\begin{array}{l}R\\ |\\ CH-COOH\\ |\\ CH_2-COOH\end{array}\right]_w-H$$

in which R is an alkyl or alkenyl radical having from 30 to 200 carbon atoms in the carbon chain and *w* is an integer having a value of between 1 to 5 inclusive.

The substituted succinic compounds may be prepared by merely reacting maleic anhydride and a polyolefin or halogenated polyolefin at temperatures in the range of 100 to 300° C. Suitable polyolefinic reactants include polyethylene, polypropylene, polybutene, polyisobutylene, polyamylene, polyisoamylene, polyisohexylene, etc. Syntheses of this type are disclosed by U.S. 3,271,295, British Patent 922,831 and U.S. 3,240,575, and a preferred preparation is described by Example 5, below.

EXAMPLE 5

One hundred and eighty parts by weight of a polyisobutylene polymer (95%, balance isoparaffins) having an average molecular weight of 890 was pre-heated to 120° F. and placed in a reactor with 43 parts by weight of maleic anhydride. The admixture was vigorously agitated until visibly homogeneous and elevated to a temperature of 560° F. over a period of 7 hours. The resultant reaction product was predominantly the substituted succinic anhydride. Approximately one-half of the reaction product was admixed with water and heated to 200° F. for a period of 4 hours to convert the anhydride to substituted succinic acid. The water was then removed by means of azeotropic distillation.

As previously noted, the foregoing substituted succinic acids and anhydrides are intermediates in relation to the practice of the invention and are further reacted with polyamines prior to their use in the invention. Such reaction is disclosed by U.S 3,271,295 and 3,271,296. Polyamines suitable as reactants include diethylene triamine, pentaethylene hexamine, 1,3-diamino propane, 1,6-diamino hexane, triethylene tetramine, ethylene diamine, propylene diamine, etc., which are represented by the formula:

$$H_2N-\left[C_xH_{2x}(CH_3)_yNH\right]_z-H$$

in which *x* is an integer having a value of between 1 to 10 inclusive, *y* is an integer having a value of zero or 1 and *z* is an integer having a value of between 1 to 10 inclusive.

Preparations of the final succinic derivative, i.e. reaction product of the substituted succinic acid or anhydride and the amine, are illustrated by Examples 6 and 7 below.

EXAMPLE 6

The substituted succinic anhydride of Example 5 (180 parts by weight) was admixed with diethylene triamine (12 parts by weight) and xylene (85 parts by weight), heated to 180° F. and maintained at that temperature for 30 minutes under reflux, and then elevated to 280° F. in order to strip off the xylene.

EXAMPLE 7

Example 6 was repeated with the substitution of 17 parts by weight of propylene diamine for the diethylene triamine, and the substitution of an equal quantity of the substituted succinic acid of Example 5 for the substituted succinic anhydride which was employed in Example 6.

In the preferred practice of the invention, the metal deactivator, phenolic compound and succinic derivative are employed in a weight ratio of 1:1.5:5. However, only economic considerations influence the use of much greater ranges of each ingredient. For example, the metal deactivator is the most costly ingredient at the present time and the limitation of quantity of this material which is employed yields a desirable cost:anti-fouling performance ratio. In addition, effective performance is realized when the inventive combination of ingredients is employed at a level of between 0.5 to 10,000 parts by weight of the inventive anti-foulant for each one million parts by weight of the material, e.g. petroleum hydrocarbon, which is treated. Preferably 5 to 100 parts per million of the anti-foulant are employed although much larger quantities may be tolerated if an increased treatment cost and/or decreased cost:anti-fouling performance ratio may be tolerated. It is also preferable to employ the inventive combination of ingredients in a weight ratio in which none of the three ingredients, e.g. metal deactivator, phenolic compound or succinic derivative, is present as a quantity of less than 10% by weight of the total anti-foulant exclusive of detergents, solvent or carriers. In the latter regard, it should be noted that the inventivve anti-foulants may be employed while dispersed in a suitable carrier. While many carriers are suitable, petroleum hydrocarbon derivatives such as kerosene or a naphtha solvent are preferred as the result of their compatibility and miscibility with the materials to be treated.

Similarly, the inventive anti-foulants may be readily added to the material to be treated by mere addition with moderate agitation. For example, their addition to a process stream at a point characterized by some flow or turbulence will facilitate their dispersion.

In regard to the efficacy of the inventive compounds as anti-foulants, studies yielding the data set forth in Table 1 were conducted. In these studies, a #2 raw fuel oil (undesulfurized light virgin furnace oil) was admixed with the specified quantities of anti-foulant agent and recycled through heated tubes having an outer diameter of ⅜ inch at the rate of 0.6 gallon per hour for a period of 20 hours. During the study, the oil exiting from the tubes was maintained at a temperature of between 530–570° F. Upon the completion of each list, the tubes, which had been weighed prior to the test, were drained, oven-dried and weighed to yield the weight of fouling deposits which had accumulated during the test.

The synergistic effect yielded by the invention, i.e., the cooperative action of the discrete ingredients yield a total effect which is greater than the sum of the effects of the ingredients, is clearly demonstrated by the foregoing data.

In the first instance, the combined ingredients (Test 6) yield a total elimination of fouling deposits, while the individual ingredients (Tests 2, 3 and 4) permit the formation of appreciable quantities of fouling deposits, despite the fact that they are employed in quantities ranging between 2 to 4 times the quantities employed in the inventive combinaiton.

Secondly, an improvement over the results (Test 5) realized by the inventor's co-pending invention (Ser. No. 595,045) is demonstrated by a comparison of the results obtained with Test 6 with the results of Test 5. Similarly, a synergistic improvement over the results realized with the copending invention is demonstrated by a comparison of the results of Test 6 with the results of Tests 4 and 5. In the first instance, the reduced fouling which is experienced with the combination of the metal deactivator and phenolic compound is completely eliminated when the same quantity of the foregoing ingredients is combined with the succinic derivative. In the second case, one-half of the quantity of the succinic derivative, and the same quantities of metal deactivator and phenolic compound (Test 6) yield the complete elimination of fouling, whereas the ingredients employed separately (Tests 4 and 5), and with much greater quantity of the succinic derivative (Test 4) yield appreciable fouling. Tests 7 and 8 have been included in Table 1 for the purpose of demonstrating that other ratios of the ingredients of the inventive compositions are also suitable and highly efficient.

TABLE 1

Test No.	Anti-foulants employed (p.p.m.)	Quantity of each anti-foulant (p.p.m.)	Total quantity of anti-foulant (p.p.m.)	Weight of fouling deposits (milli-grams)
1 (control).	0	0	0	566
2	Metal deactivator [1]	5	5	328
3	Phenolic compound [2]	15	15	435
4	Succinic derivative [3]	25	25	55
5	Metal deactivator [1]	2.5	6.25	103
	Phenolic compound [2]	3.75		
6	Metal deactivator [1]	2.5	18.75	0
	Phenolic compound [2]	3.75		
	Succinic derivative [3]	12.5		
7	Metal deactivator [1]	3.3	16.3	15
	Phenolic compound [2]	5.0		
	Succinic derivative [3]	8.0		
8	Metal deactivator [1]	4	15	6
	Phenolic compound [2]	6		
	Succinic derivative [3]	5		

[1] N,N'-disalicylidene-1,2-propanediamine.
[2] Phenolic condensate of Example 3.
[3] Reaction product of Example 6.

Furthermore, the inventive compositions demonstrate an efficacy at high temperatures which has not been yielded by previous anti-foulants. This improvement is significant in that satisfactory anti-foulants have not previously been available for processes, employing higher temperatures. This improvement is demonstrated by Table 2 which contrasts the inventive compositions with standard commercial anti-foulants in tests simliar to those of Table 1 in which the skin temperature of the tubes through which the oil was cycled ranged between 740–780° F. at the exiting end of the tube.

TABLE 2

Test	Anti-foulant	Quantity of anti-foulant (p.p.m.)	Quantity of fouling deposits (mgs.)
A	Commercial antifoulant No. 1	100	318
B	Commercial antifoulant No. 2	100	159
C	Composition of Test No. 6 on Table 1	18.75	0

In relation to Table 2, it should be noted that the inventive composition completely eliminated fouling deposits while the standard commercial anti-foulants, even though employed in quantities 5 times as great, permitted the formation of substantial fouling deposits.

Finally, the inventive products also yield a substantial heat transfer improvement. Specifically, the U value (average final heat transfer coefficient in B.t.u./°F-ft.$_2$-hr.) demonstrated a substantial improvement in the tests previously discussed. For example, the inventive composition employed in Test 6 of Table 1 yielded a heat transfer value which represented a 71% improvement of the control (devoid of anti-foulant) with which it was contrasted.

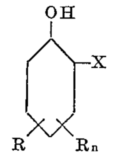
It is apparent that various compositions and methods for the treatment of liquid petroleum hydrocarbons have been provided, that such methods and compositions provide effective control over the formation of fouling deposits as well as losses in heat transfer, that such control represents a substantial improvement over the prior art and a synergistic improvement over the results obtainable with the individual ingredients of the inventive compositions, and particularly over the results obtainable at temperatures in excess of 500° F., and that low cost, effective methods and materials are therefore provided.

It is also obvious that various alterations, substitutions and modifications of the methods and compositions of the present invention may be adopted without departing from the spirit of the invention as defined by the following claims.

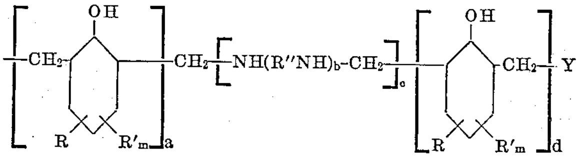
I claim:

1. A method for controlling the formation of fouling deposits in petroleum hydrocarbon during processing at elevated temperatures, comprising dispersing within said

hydrocarbon an anti-foulant comprising the combination of (I) a phenolic compound having the formula



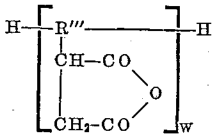
in which R is an alkyl group attached to a carbon atom of the aromatic ring and contains between 4 to 12 carbon atoms, *n* is an integer having a value of between zero to 1 inclusive, and X is a substituent selected from the group consisting of hydrogen and a phenolic group having the formula



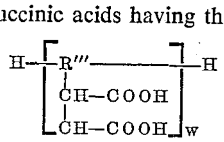
in which R′ is an alkyl group attached to a carbon atom of the aromatic ring and contains between 4 to 12 carbon atoms, R″ is a divalent hydrocarbon radical containing between 1 to 4 carbon atoms inclusive, Y is selected from the group consisting of hydroxyl and alkyl phenol, *a* and *d* are integers having a value of between zero to 15 inclusive, *m* and *c* are integers having a value of between zero to 1 inclusive, *b* is an integer having a value of between zero to 4 inclusive, and the sum total of *a* and *d* is no mode than 25, (II) the reaction product of a polyamine having the formula

$$H_2N\left[C_xH_{2x}(CH_3)_yNH\right]_zH$$

in which *x* is an integer having a value of between 1 to 10 inclusive, *y* is an integer having a value of between zero to 1 inclusive, and *z* is an integer having a value of between 1 to 10 inclusive, and a succinic compound selected from the group consisting of substituted succinic anhydrides having the formula



and substituted succinic acids having the formula

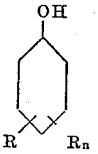


in which R‴ is selected from the group consisting of alkyl and alkenyl radicals having between 30 to 200 carbon atoms inclusive in the carbon chain and *w* is an integer having a value of between 1 to 5 inclusive, and (III) N,N′-disalicylidene-1,2-propane diamine.

2. A method as claimed by claim **1** in which said phenolic compound, said reaction product and said N,N′-disalicylidene-1,2-propane diamine are all present in quantity which is at least equal to 10% of the total weight of said anti-foulant.

3. A method as claimed by claim **1** in which between 0.5 to 10,000 parts by weight of said anti-foulant are dispersed in each one million parts by weight of said petroleum hydrocarbon.

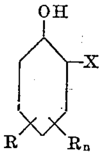
4. A method as claimed by claim **1** in which said phenolic compound is the condensate of formaldehyde, a nitrogen containing compound and an alkyl phenol having the formula



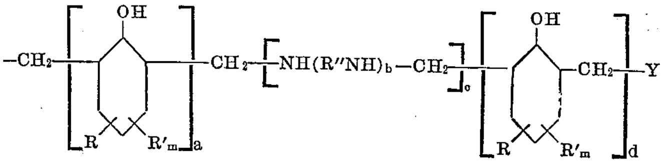
in which R is an alkyl group attached to a carbon atom of the aromatic ring of said phenol and contains between 4 to 12 carbon atoms inclusive, and *n* is an integer having a value of between zero to 1 inclusive.

5. A method as claimed by claim **4** in which said nitrogen containing compound is selected from the group consisting of ammonium hydroxide, ethylene diamine, propylene diamine and 1,3 diamino propane.

6. An anti-foulant composition consisting essentially of (I) a phenolic compound having the formula



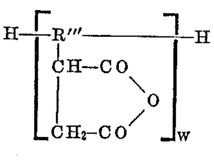
in which R is an alkyl group attached to a carbon atom of the aromatic ring and contains between 4 to 12 carbon atoms, *n* is an integer having a value of between zero to 1 inclusive, and X is a substituent selected from the group consisting of hydrogen and a phenolic group having the formula



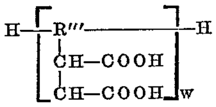
in which R′ is an alkyl group attached to a carbon atom of the aromatic ring and contains between 4 to 12 carbon atombs, R″ is a divalent hydrocarbon radical containing between 1 to 4 carbon atoms inclusive, Y is selected from the group consisting of hydroxyl and alkyl phenol, *a* and *d* are integers having a value of between zero to 15 inclusive, *m* and *c* are integers having a value of between zero to 1 inclusive, *b* is an integer having a value of between zero to 4 inclusive, and the sum total of *a* and *d* is no more than 25, (II) the reaction product of a polyamine having the formula

$$H_2N\left[C_xH_{2x}(CH_3)_yNH\right]_zH$$

in which *x* is an integer having a value of between 1 to 10 inclusive, *y* is an integer having a value of between zero to 1 inclusive, and *z* is an integer having a value of between 1 to 10 inclusive, and a succinic compound selected from the group consisting of substituted succinic anhydrides having the formula



and substituted succinic acids having the formula

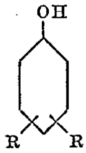


$$H{-}\left[\begin{array}{l}R'''{-}\\ \;|\\ CH{-}COOH\\ \;|\\ CH{-}COOH\end{array}\right]_w{-}H$$

in which R''' is selected from the group consisting of alkyl and alkenyl radicals having between 30 to 200 carbon atoms inclusive in the carbon chain and *w* is an integer having a value of between 1 to 5 inclusive, and (III) N,N'-disalicylidene-1,2-propane diamine in which said phenolic compound, said reaction product and said N,N'-disalicylidene-1,2-propane-diamine are each present in a quantity which is at least equal to 10% of the total weight of said anti-foulant.

7. A composition as claimed by claim **6** in which said phenolic compound is present in a quantity of between 0.5 to 3 parts by weight for each part by weight of said N,N'-disalicylidene-1,2-propane.

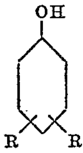
8. A composition as claimed by claim **6** in which said phenolic compound is the condensate of formaldehyde, a nitrogen containing compound and an alkyl phenol having the formula



in which R is an alkyl group attached to a carbon atom of the aromatic ring of said phenol and contains between 4 to 12 carbon atoms inclusive, and *n* is an integer having a value of between zero to 1 inclusive.

9. A composition as claimed by claim **8** in which said nitrogen containing compound is selected from the group consisting of ammonium hydroxide, ethylene diamine, propylene diamine and 1,3 diamino propane.

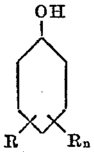
10. A composition as claimed by claim **6** in which said phenolic compound is alkyl phenol having the formula



in which R is an alkyl group attached to a carbon atom of the aromatic ring of said phenol and contains between 4 to 12 carbon atoms inclusive, and *n* is an integer having a value of between zero to 1 inclusive.

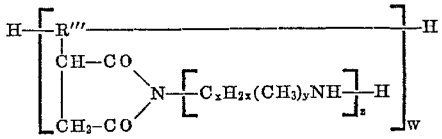
11. A composition as claimed by claim **6** in which said alkyl phenol is t-octyl phenol.

12. A composition as claimed by claim **6** in which said phenolic compound is the condensate of formaldehyde and alkyl phenol having the formula



in which R is an alkyl group attached to a carbon atom of the aromatic ring of said phenol and contains between 4 to 12 carbon atoms inclusive, and *n* is an integer having a value of between zero and 1 inclusive.

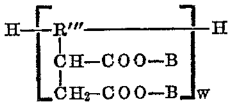
13. A composition as claimed by claim **6** in which said reaction product has the formula



$$H{-}\left[\begin{array}{l}R'''{-}\\ \;|\\ CH{-}CO\\ \;|\qquad\quad \searrow\\ \;|\qquad\qquad N{-}\left[C_xH_{2x}(CH_3)_yNH\right]_z{-}H\\ \;|\qquad\quad \nearrow\\ CH_2{-}CO\end{array}\right]_w{-}H$$

in which R''' is selected from the group consisting of alkyl and alkenyl radicals having between 30 to 200 carbon atoms inclusive in the carbon chain, *w* is an integer having a value of between 1 to 5 inclusive, *x* and *z* are integers having a value of between 1 to 10 inclusive, and *y* is an integer having a value of between zero to 1 inclusive.

14. A composition as claimed by claim **6** in which said reactant product has the formula



$$H{-}\left[\begin{array}{l}R'''{-}\\ \;|\\ CH{-}COO{-}B\\ \;|\\ CH_2{-}COO{-}B\end{array}\right]_w{-}H$$

in which R''' is selected from the group consisting of alkyl and alkenyl radicals having between 30 to 200 carbon atoms inclusive, *w* is an integer having a value of between 1 to 5 inclusive, B is selected from the group consisting of hydrogen and

$$-\left[C_xH_{2x}(CH_3)_yNH\right]_z{-}H$$

in which *x* and *z* are integers having a value of between 1 to 10 inclusive, and *y* is an integer having a value of between zero to 1 inclusive.

15. A composition as claimed by claim **6** in which said polyamine is selected from the group consisting of diethylene triamine, pentaethylene hexamine, 1,3-diamino propane, 1,6-diamino hexane, triethylene tetramine, ethylene diamine, and propylene diamine.

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DELBERT E. GANTZ, *Primary Examiner.*

G. E. SCHMITKONS, *Assistant Examiner.*