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ANTI-FOULANT AGENTS FOR PETROLEUM HYDROCARBONS

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15 Claims

ABSTRACT OF THE DISCLOSURE

Synergistic binary antifoulant additive for petroleum hydrocarbon streams subjected to elevated temperatures, e.g., heat exchangers, is the conventional metal deactivator, disalicylidene propane diamine, and a nalkylphenol or alkylphenol-formaldehyde condensate. Laboratory fouling tests using raw virgin furnace oil showed negligible antifoulant benefit for the phenol condensate alone and moderate benefit for deactivator alone. Excellent antifouling was obtained with the binary combination at deactivator/phenolic ratios in range of 1/0.5–1/2 and dosages of 1–20 p.p.m.

The present invention concerns anti-foulants for use in petroleum hydrocarbon streams and feedstocks which are subjected to elevated temperatures, and methods for preventing the deposition of fouling deposits within such streams and feedstocks upon exposure to elevated temperatures, and particularly concerns anti-foulants which contain the combination of a metal deactivator and a phenolic compound.

In the processing of petroleum hydrocarbons and feedstocks such as petroleum processing intermediates, petrochemical intermediates, e.g., gas oils and reformer stocks, the hydrocarbons are commonly heated to temperatures in excess of 250° F. Similarly, such petroleum hydrocarbons are frequently employed as heating mediums on the "hot side" of heating and heat exchange systems. In both instances, the petroleum hydrocarbon liquids are subjected to elevated temperatures which produce a separate phase known as fouling deposits, within the petroleum hydrocarbon. In all cases, these deposits are undesirable by-products. In many processes, the deposits reduce the bore 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 available surfaces to restrict heat transfer and necessitate frequent shut-downs for cleaning, increased processing cycles or increased coolant flow, or both.

While the nature of the foregoing deposits defies precise analysis, they appear to contain both carbonaceous phases of a coke-like nature, and polymers or condensates formed from the petroleum hydrocarbons or impurities present therein. The catalysis of such condensates has been attributed to metal compounds such as copper or iron which are present as impurities. For example, such metals may accelerate the hydrocarbon oxidation rate by promoting degenerative chain branching, and the resultant free radicals initiate oxidation and polymerization reactions which form gums and sediments. It further appears that the relatively inert carbonaecous deposits are entrained by the more adherent condensates or polymers to thereby contribute to the insulating or thermal opacifying effect.

Previous attempts to reduce or eliminate the formation of fouling deposits in such environments have employed phenolic compounds which are believed to break the chain of anti-fouling deposits by yielding an anti-oxidant effect.

It is an object of the present invention to provide anti-

foulants which greatly reduce fouling deposits in liquid petroleum hydrocarbons during the exposure of such hydrocarbons to elevated temperatures.

A further object is the provision of anti-foulants which reduce the formation of deposits and coatings which impede heat transfers.

Another object is the provision of anti-foulants which are effective in the control of sludge formation and heat transfer impeding deposits, at low concentrations.

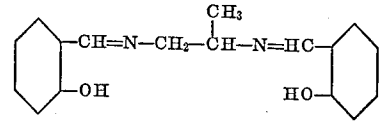
An additional object is the provision of low cost anti-foulants both as the result of the reduction of the total quantity of anti-foulant required, and the reduction of the quantities of costly metal deactivators which are required.

Still another object is the provision of methods for reducing the formation of sludge and heat transfer impeding deposits in liquid petroleum hydrocarbons during the exposure of such hydrocarbons to elevated temperatures.

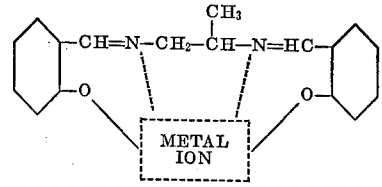
These and other objects will become apparent from an examination of the specification and claims, and are achieved by means of a synergistic combination of ingredients.

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 qantity of anti-foulant required, represents a substantial improvement over the anti-foulant agents of the prior art.

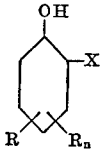
The metal deactivator employed in the practice of the present invention is N,N'-disalicylidene-1,2-propanediamine, having the formula:



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:

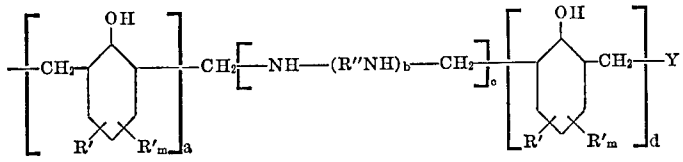


The phenolic compounds which are utilized in the practice of the invention are mono and dialkyl substituted phenols, and the condensates of such phenols, including nitrogen containing phenolic condensates. These phenolic compounds and condensates may be represented by the formula:



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.

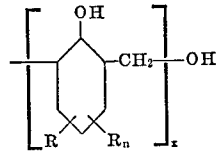
It should be noted that the alkyl substituents R and R' are probably the primary factor contributing to the hydrocarbon solubility or dispersibility of these phenolic compounds and condensates. This solubility, when enhanced by the synergistic activity which is realized when the phenolic compounds are 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 non-condensed 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 non-condensed 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 co-reactant 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 volatility 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 of 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 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.

In the practice of the invention, the phenolic compound and the metal deactivator may be merely admixed or blended and added to the system to be treated. However, for many applications, a dispersion of these two compounds in an oil soluble or miscible carrier, e.g., kerosene, xylene, etc. is desirable. In such applications a 15 to 80% solution of the combined active ingredients has proved satisfactory results, although higher or lower concentrations are both feasible and operable.

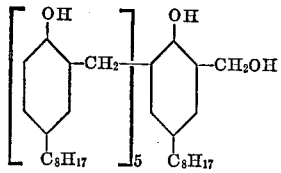
For purposes of economy, and in the interests of obtaining the highest degree of efficiency in relation to the quantity of anti-foulant employed, between 0.5 to 100 parts by combined weight of the metal deactivator and phenolic compound are preferably employed for each one million parts by weight of the petroleum hydrocarbon which is treated. However, treating levels as low as 0.1 p.p.m. have been satisfactorily employed, and there is no reason to doubt that even higher concentrations would yield increased, if less efficient, results in the absence of

economic considerations. However, some "trial and error" may be required in determining a satisfactory treating level, due to the varying fouling potentials of different hydrocarbons. The metal deactivator and phenolic compound are preferably employed in a ratio of 1:0.5–3 parts by weight. However, ratios as high as 1:6 and as low as 1:0.1 have been satisfactorily utilized. Naturally, both the treating level employed, and the metal deactivator:phenolic compound ratio may be influenced by the nature of the hydrocarbon to be treated.

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.

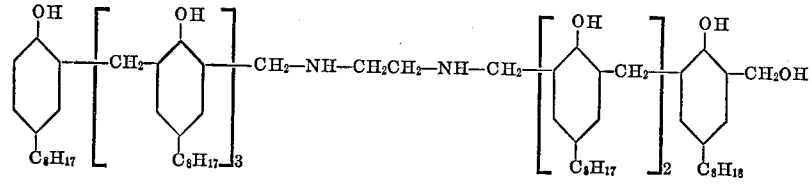
EXAMPLE 2

The reaction of Example 1 was repeated with a 0.6:1:0.8 ratio of octyl phenol:formaledhyde: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.

The anti-fouling effect obtained with the compositions of the invention, and the contrast between these results and the anti-fouling effect achieved with the individual ingredients of the inventive combinations, are shown by Table 1, below. The results include three different concentrations of a 2:3 admixture of N,N'-disalicyclidene-1,2-propane diamine and the phenol-formaldehyde condensate of Example 1. The anti-fouling effect represents the percentage reduction in foulant formation which was achieved with samples C–E as contrasted with control samples of the same petroleum hydrocarbon which were devoid of the inventive combination but which did contain one or the other of the two ingredients employed in the inventive combination (samples A and B). To obtain these results each sample, and the control for each sample, were passed through two heated tubes having an outer diameter of ⅜ inches, and a length of 18 inches, at the rate of 0.6 gallon per hour. The two heated tubes were connected in series and the exit temperature of the petroleum hydrocarbon was maintained at 500° F. In all cases, a total of 12 gallons of each sample and each control was passed through the tubes during a 20 hour period. The high temperature and relatively long dwell time were employed to induce the formation of fouling deposits. In each case, a #2 raw fuel oil (light virgin furnace oil) which is commonly employed as the feed or influent to dehydrotreating and desulfurizing units, was employed as both the control and the petroleum hydrocarbon to which the treating materials were added. The clean tubes were weighed before each run and upon the completion of each trial the tubes were drained, oven-dried, weighed and the tare was noted. The weight increase in the tubes through which the control hydrocarbons were processed, and the tubes through which the hydrocarbons containing an antifoulant were processed, were then compared to yield the percentage of reduction in fouling deposits accumulated in the tubes.

The theoretical or additive effect of the individual ingredients of the multiple ingredient treating compositions was derived by computing the anti-fouling effect yielded by each part per million of each ingredient employed in each composition, multiplying this factor by the number of parts per million of the ingredients which were employed, and totalling the theoretical effect of both ingredients. For example, 5 parts per million of the deactivator yield an anti-fouling effect of 33.7, so each p.p.m. of the deactivator contributes an anti-fouling effect of 33.7/5, or 6.7. Similarly, 5 p.p.m.s. of the phenolic condensate provide no anti-fouling effect, so that each p.p.m. of the condensate contributes an anti-fouling effect of 0/5, or zero. In the case of sample D, 2.4 p.p.m. of deactivator were employed, with each p.p.m. of deactivator contributing an anti-fouling effect of 6.7. Consequently, the deactivator content of that sample should provide an anti-fouling effect of 16 (2.4×6.7). Since the phenolic condensate portion of that sample is incapable of providing

an anti-fouling effect, the theoretical anti-fouling effect of the combined ingredients is 16+0, or 16.

TABLE I

Sample	Total quantity of anti-foulant added to the petroleum hydrocarbon (p.p.m.)	Total quantity of metal deactivator present in the petroleum hydrocarbon (p.p.m.)	Total quantity of phenolic condensate (p.p.m.)	Theoretical or additive anti-fouling effect which should be provided by the multiple ingredients (percent reduction in fouling deposits)	Actual anti-fouling effect obtained (percent reduction in fouling deposits)
A	5	0	5	----------	0
B	5	5	0	----------	33.7
C	3	1.2	1.8	8	37.4
D	6	2.4	3.6	16	97.8
E	9	3.6	5.4	24	100

The theoretical or additive anti-fouling effect was employed in the above table in order to clearly demonstrate the synergistic effect which is provided by the inventive compositions. For example in the case of sample D an anti-fouling effect of 16 would be anticipated in the absence of synergism, and if the contribution of the individual ingredients was merely additive. Instead, an anti-fouling effect of 97.8 was achieved, and this effect represents a 611% increase over the predictable or theoretical result which would be expected. Comparable synergistic showings were obtained with various combinations of the condensates of Examples 2–4, as well as the other phenolic compounds and condensates of the invention.

A further example of the general efficacy of the invention is provided by Table 1–B below, which shows the actual quantity of fouling deposits realized with various levels of different inventive compositions, as contrasted with an untreated control. These tests were also conducted by the method described in relation to Table 1, and employed the same metal deactivator.

TABLE 1-B

Quantity of metal deactivator (p.p.m.)	Molar ratio of the constituents of the condensate				Quantity of condensate (p.p.m.)	Quantity of fouling deposits (mg.)
	t-Octyl phenol	Formaldehyde	Ammonium hydroxide	Ethylene diamine		
0	0	0	0	0	0	160
0.8	1.5	1	2	0	1.60	27
1.25	1.5	1	2	0	2.50	10
2.50	1.5	1	2	0	3.60	10
2.50	1.5	1	2	0	5.00	11
2.50	1.5	1	2	0	1.70	4
3.60	1.5	1	2	0	5.40	0
5.00	1.5	1	2	0	7.50	14
5.00	1.5	1	2	0	10.00	7
6.00	1.5	1	2	0	9.00	0
10.00	1.5	1	2	0	10.00	0
2.5	4	4	0	1	1.10	9
2.5	4	4	0	1	2.20	30
5	4	4	0	1	4.50	12

The effectiveness of small quantities of the inventive compositions, as well as the suitability of various ratios of metal deactivators and phenolic compounds, is demonstrated by Table 2 in which the results were achieved by means of the same method employed in respect to Table 1:

TABLE 2

Sample	Total quantity of anti-foulant (p.p.m.)	Deactivator: condensate ratio	Theoretical anti-fouling effect (percent reduction in fouling deposits)	Actual anti-fouling effect obtained (reduction fouling deposits)
F	3.75	1:2	8.375	93.7
G	2.40	1:2	5.4	82.8
H	1.92	1:0.67	8.375	72.9
J	4.18	1:0.67	16.75	97.5
K	9.00	1:1.5	24.0	100

The above data are based upon trials conducted with N,N'-disalicycledene-1,2-propane diamine and the phenolic condensate of Example 1.

As previously stated, phenolic compounds other than the condensates of Examples 1–4 may also be employed. The effectiveness of one of these compounds, i.e., t-octyl phenol, is demonstrated by Table 3 which employs a 1:1.2 ratio of the metal deactivator (N,N'-disalicylidine-1,2-propane diamine) and the t-octyl phenol in the same type of test as was described in respect to the showings of Table 1.

TABLE 3

Sample	Total quantity of treatment employed (p.p.m.)	Quantity of metal deactivator (p.p.m.)	Quantity of t-octyl phenol (p.p.m.)	Anti-fouling effect (percent reduction in fouling deposits)
L	2.75	1.25	1.5	77.7
M	5.5	2.5	3.0	97.6

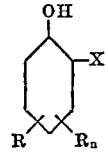
Comparable results are also possible with various combinations of the metal deactivator with nonyl phenol, dioctyl phenol and t-butyl phenol and the condensates of these alkyl phenols.

It is apparent that various compositions and methods for the treatment of liquid petroleum hydrocarbons have been provided and that such compositions and methods provide the inhibition of the formation of fouling deposits in such hydrocarbons at high temperatures, while permitting the use of low concentrations of the anti-foulant, and appreciable reductions in cost.

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:

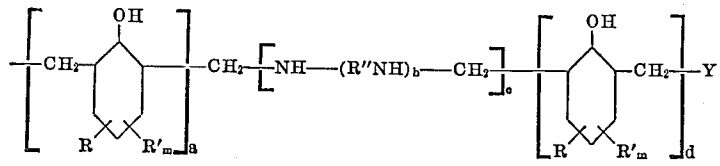
I claim:

1. A method for reducing the quantity of fouling deposits formed by a petroleum hydrocarbon during processing at elevated temperatures, comprising adding to said hydrocarbon the combination of N,N'-disalicylidene-1,2-propane diamine and 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, and X is a substituent selected from the group consisting of hydrogen and a phenolic group having the formula

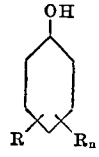


in which R' is an alkyl group attached to a carbon atom of the aromatic ring and contains between 4 to 12 carbon atoms, R'' is a divalent hydrocarbon radical containing between 1 to 4 carbon atoms, Y is selected from the group consisting of hydroxyl and alkyl phenol, *a* and *d* are integers having a value of between zero to 15, *m* and *c* are integers having a value of between zero to 1, *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.

2. A method as claimed by claim **1** in which said combination is added in a quantity of between 0.5 to 100 parts by weight for each one million parts by weight of said hydrocarbon.

3. A method as claimed by claim **1** in which said combination contains between 0.5 to 3 parts by weight of said phenolic compound for each part by weight of said propane diamine.

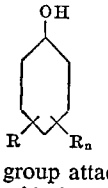
4. A method as claimed by claim **1** in which said phenolic compound is the condensate of formaldehyde, alkyl phenol having the formula:



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 and *n* is an integer having a value of between zero to 1, and a nitrogen containing compound.

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.

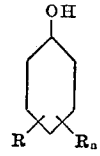
6. A method as claimed by claim **1** in which said phenolic compound is alkyl phenol having the formula:



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 and *n* is an integer having a value of between zero to 1.

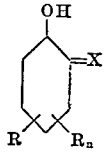
7. A method as claimed by claim **1** in which said phenolic compound is t-octyl phenol.

8. A method as claimed by claim **1** in which said phenolic compound is the condensate of formaldehyde and alkyl phenol having the formula:

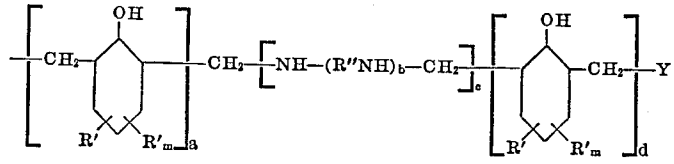


in which R is an alkyl group attached to a carbon atom of the aromatic ring of said phenol and contains between 4 to 12 carbon atoms, and *n* is an integrer having a value of between zero to 1.

9. A composition for reducing the quantity of fouling deposits formed by a petroleum hydrocarbon during processing at elevated temperatures, consisting essentially of an admixture of one part by weight of N,N'-disalicylidene-1,2-propanediamine and a phenolic compound having the formula:



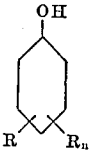
in which R is an alkyl group attached to a carbon atom of the aromatic ring and contains between 4 to 12 carbon atoms, *n* is an integer having a value of between zero to 1, and *x* is a substituent selected from the group consisting of hydrogen and a phenolic group having the formula:



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, 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 1, *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.

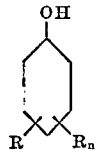
10. A composition as claimed by claim **9** in which said combination contains between 0.1 to 6 parts by weight of said phenolic compound for each part by weight of said propane diamine.

11. A composition as claimed by claim **9** 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 and *n* is an integer having a value of between zero to 1.

12. A composition as claimed by claim **9** in which said phenolic compound is the condensate of formaldehyde, alkyl phenol having the formula:

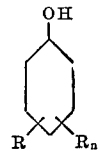


in which R is an alkyl group attached to a carbon atom of the aromatic ring of said phenol and contains between 4 to 12 carbon atoms and *n* is an integer having a value of between zero to 1, and a nitrogen containing compound.

13. A composition as claimed by claim **12** in which said nitrogen containing compound is selected from the group consisting of ammonium hydroxide, ethylene diamine, propylene diamine and 1,3-diamine propane.

14. A composition as claimed by claim **9** in which said phenolic compound is t-octyl phenol.

15. A composition as claimed by claim **9** 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 *n* is an integer having a value of between zero to 1.

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