

# UNITED STATES PATENT OFFICE

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## HYDROCARBON FUEL BLENDS

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This invention deals with a method of treating fuels with a corrosion inhibiting additive to render the fuels non-corrosive to metals and, in general, to counteract objectionable effects arising from unstable sulfur-containing compounds present in fuel compositions.

The corrosion inhibiting additive used in accordance with the present invention is characterized by phenol sulfide type compounds which I have discovered to be surprisingly effective as corrosion inhibitors in petroleum fuel products when incorporated therein in certain restricted amounts.

Hydrocarbon fuels of various types, including gasoline, heating oils, and Diesel fuels, are required to meet A. S. T. M. specifications on tolerance limits of corrosiveness, because it is desirable to avoid internal corrosion of pipes, storage tanks, refinery equipment, fuel supply containers, and engine or burner parts with which the fuels come into contact during handling and use. Generally, the metals contacted by the fuels are constructed of iron and copper, their alloys, and similar metals which are highly susceptible to corrosion believed to result mainly from the action of unstable or reactive sulfur-containing compounds ordinarily present in mineral fuel oils, except when the fuels have been extremely well refined.

It has also been found that water white petroleum distillates employed as fuels, even after very careful refining, may contain small amounts of unstable compounds of sulfur which tend to cause discoloration of the oil during storage, and more intensely when exposed to sunlight.

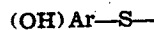
It has been found that in gasoline the corrosive sulfur-containing compounds are detrimental to the anti-knock quality of the fuel, particularly when the fuel is treated with lead alkyl anti-knock agents. While in the case of Diesel fuels, although certain corrosive sulfur-containing compounds are beneficial to the ignition quality of the fuel in a compression-ignition engine, it is also desirable to reduce the corrosiveness of these fuels without impairing their ignition quality.

The effects of corrosiveness and instability are very undesirable and necessitate special and expensive processing methods to produce saleable fuel products, unless these effects can be suitably

counteracted by an economical additive, such as those herein provided.

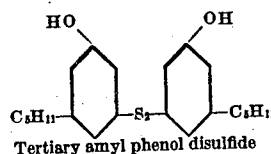
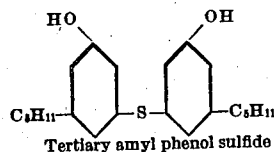
Thus, while it is the main object of this invention to reduce the corrosiveness of various types of fuels, it also embraces the use of a corrosion inhibiting additive which can be employed with benefit or without detriment to combustion qualities of various fuels.

The class of corrosion inhibiting additive found to accomplish the objects set forth in accordance with the present invention includes compounds which characteristically contain the hydroxy-aryl-sulfide group represented by the following formula:



wherein Ar is an aryl nucleus containing a hydroxy (OH) substituent, and S represents a sulfur substituent in the aryl nucleus. In the preferred alkylated phenol sulfides for the present purposes, alkyl side chain substituents are present in the aryl nuclei, including alkyl groups containing from about 3 to 6 carbon atoms, e. g., propyl, butyl, amyl, and hexyl radicals, and the substituted aryl nuclei are linked together through sulfur in a sulfide group.

Representative examples of this class of compounds are the following:



40 Many other compounds having the characteristic grouping of these compounds may be employed with modifications, such as the introduction of amino substituents or other groups into the aryl nuclei or side chains, and replacements of hydrogen in the hydroxy groups by atoms or groups, such as metals or alkyl groups, in what can be defined generically as being oxy-aryl sulfides.

45 A procedure of forming the sulfides is as fol-

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lows: A mol proportion of an alkylated phenol is dissolved in an inert diluent, such as ethylene dichloride ( $\text{CH}_2\text{ClCH}_2\text{Cl}$ ), and the solution is heated to boiling under reflux. Then a  $\frac{1}{2}$  mol proportion of sulfur monochloride ( $\text{S}_2\text{Cl}_2$ ) in the diluent is added slowly with stirring to the boiling solution of the alkylated phenol. The hydrogen chloride gas evolved during the reaction is withdrawn from the reaction zone through the reflux condenser. When the addition of the sulfur monochloride solution is completed, the boiling of the reaction mixture is continued for a period until no further effusion of hydrogen chloride occurs. The time of refluxing can be shortened by passing an inert gas, such as nitrogen, through the reaction mixture. The diluent and any unreacted material is removed from the reaction product by distillation under vacuum at a temperature maintained preferably below about  $150^\circ\text{C}$ .

By substituting sulfur dichloride for the sulfur monochloride in the process described, instead of the disulfide linkage, a monosulfide or thioether linkage is obtained. The organic reactant may be dicyclic, as in the case of naphthols, an unsaturated aliphatic compound may be made to react with the phenol, and the phenol reactant may be modified, as indicated, e. g., to form alkoxy aryl sulfides.

Other configurations may result, depending upon the initial configuration of the alkylated phenol and effects of the reaction used in preparing the sulfides.

While it is true that compounds of this type have been recommended to be useful anti-oxidants for lubricating oils when incorporated into lubricating oils in amounts ranging from about 0.1% upwardly, it had never been foreseen that compounds of this nature containing sulfur constituents could be effectively used as corrosion inhibitors in fuels. However, it is important to note that when the alkyl phenol sulfides are employed in accordance with the present invention as corrosion inhibitors, they must be used in

Free sulfur and a number of inorganic and organic compounds containing sulfur have been found to be powerful ignition promoters, but most of these substances tend to make the Diesel fuel unduly corrosive. Examples of these substances are nitrogen tetrasulfide and organic polysulfides, such as dialkyl tetrasulfides.

The effectiveness of the phenol sulfides as corrosion inhibitors is illustrated by tests on the following fuels: (1) gasoline containing 8 mg. corrosive sulfur per 100 ml.; (2) air-blown heavy heating oil or Diesel fuel containing 20 mg. corrosive sulfur per 100 ml.; and (3) Colombian gas oil, Diesel fuel stock, with and without nitrogen tetrasulfide added as an ignition promoter. The A. S. T. M. Standards test for corrosion was used.

TABLE 1  
Effects of inhibitors

Fuel tested	Inhibitor added per 100 ml. of fuel	A. S. T. M. copper strip corrosion 1 hr. at $212^\circ\text{F}$ .
Gasoline.....	None.....	Fails.
Do.....	10 mg. ter-amyl phenol sulfide.	Passes.
Do.....	10 mg. ter-amyl phenol disulfide.	Do.
Air-blown heavy fuel.....	None.....	Fails.
Do.....	10 mg. ter-amyl phenol sulfide.	Passes.
Do.....	10 mg. ter-amyl phenol disulfide.	Do.
Colombian gas oil.....	None.....	Passes.
Colombian gas oil + 0.1% $\text{N}_4\text{S}_4$ .....	do.....	Fails.
Colombian gas oil + 0.1% $\text{N}_4\text{S}_4$ .....	10 mg. ter-amyl phenol sulfide.	Passes.
Colombian gas oil + 0.1% $\text{N}_4\text{S}_4$ .....	20 mg. ter-amyl phenol disulfide.	Do.

It can be appreciated that the inhibitors featured by the present invention act in an astonishing manner to arrest corrosiveness, since these compounds themselves contain sulfur and have hitherto been regarded as corrosive materials. It is further evident that the quantity of these materials used to inhibit corrosion is critical, as is illustrated in the following tables:

TABLE 2  
Effect of tertiary amyl phenol sulfide on gasoline (containing 8 mg. corrosive sulfur/100 ml.)

Fuel tested	Corrosive gasoline clear	Inhibitor added		
		3 mg./100 ml.	10 mg./100 ml.	20 mg./100 ml.
Copper strip corr. test at $212^\circ\text{F}$ ..				
20 min.....	Passes.....	Passes.....	Passes.....	Passes.
40 min.....	B. P. <sup>1</sup> .....	do.....	do.....	Do.
60 min.....	Fails.....	do.....	do.....	Do.
80 min.....	do.....	B. P. <sup>1</sup> .....	do.....	Do.
100 min.....	do.....	Fails.....	do.....	B. P. <sup>1</sup>

<sup>1</sup> Barely passes.

critically lower proportions than when they are used as effective anti-oxidants in a lubricating oil, for otherwise they tend to actually increase the corrosiveness of the fuel. The effective corrosive inhibiting amounts of the alkyl phenol sulfides are less than 0.05% by weight and preferably in the range of from about 0.03% to about 0.003% by weight of the fuel blend.

When the phenolic sulfide corrosion inhibitors are employed to improve Diesel fuel compositions in reducing corrosiveness, they are beneficial in reducing corrosiveness imparted to the fuel by sulfur-containing ignition promoters without impairing the effectiveness of these promoters.

The foregoing data illustrates how the inhibitor was found to be most effective in the proportion of about 10 mg. per 100 ml. of the fuel and how it loses the desired effectiveness as the proportion goes outside preferred limits in the range from about 0.003% to 0.03%. The same kinds of results are evident when the disulfide inhibitor is used, except that the monosulfide is more effective, and the effectiveness of the inhibitors varies somewhat with the type of fuel stock in which they are used.

It can also be noted that the less drastic A. S. T. M. copper strip corrosion test at  $122^\circ\text{F}$ . shows up the effectiveness of these inhibitors

to even a greater advantage, as in the following table:

the scope of the invention. Any modification or variation which conforms to the spirit of the

TABLE 3

*Effect of tertiary amyl phenol disulfide as inhibitor on corrosive Diesel fuel containing a corrosive ignition promoter*

Fuel tested	Diesel fuel +0.1% N <sub>4</sub> S <sub>4</sub>	Inhibitor added		
		1 mg./100 ml.	3 mg./100 ml.	5 mg./100 ml.
A. S. T. M. copper strip test at 122° F.:				
1 hour.....	Fails.....	Passes.....	Passes.....	Passes.
2 hours.....	do.....	do.....	do.....	Do.
3 hours.....	do.....	do.....	do.....	Do.
4 hours.....	do.....	B. P. <sup>1</sup> .....	do.....	Do.
5 hours.....	do.....	Fails.....	B. P. <sup>1</sup> .....	Do.
6 hours.....	do.....	do.....	Fails.....	B. P. <sup>1</sup>

<sup>1</sup> Barely passes.

The addition of 0.1% by weight of N<sub>4</sub>S<sub>4</sub> to the Colombian gas oil increased its cetane number from 38 to 41.3, which increase was satisfactorily maintained with the addition of the inhibitor.

In preparing the Diesel fuel compositions of reduced corrosiveness, any hydrocarbon oil suitable as a fuel base for Diesel engines may be used. Ordinarily, the Diesel hydrocarbon fuel base employed has a boiling range above that of gasoline, and, more particularly, has a boiling range and viscosity corresponding to that of heavy kerosene or gas oil distillates which boil from about 375° F. to about 700° F. In some instances, a more narrowly cut fraction, such as one distilling from about 375° F. to 600° F., may be used. The corrosive types of ignition promoter compounds are generally added to the Diesel fuel in small proportions of less than about 5% by weight. Extremely potent ignition promoters, such as nitrogen tetrasulfide (N<sub>4</sub>S<sub>4</sub>) and free sulfur are generally added in smaller quantities of about 0.1% to 0.5%.

The exact quantity of the phenol sulfide type corrosion inhibitor used in the fuel compositions depends upon the extent to which it is desired that the corrosion be eliminated, the amounts and kinds of materials present in the fuel composition, the temperature and length of storage, but in any event, the proportion of this type of corrosion inhibitor should not be substantially outside the range of 0.001% to 0.05% by weight.

In utilizing the present invention for diminishing corrosiveness of corrosive gasolines, the gasoline fuel stock to which the inhibitor is added may be a petroleum distillate, liquefied petroleum gases, or a synthetic fuel which has not been subjected to extensive refining so that the fuel contains more than 4 mg. of reactive sulfur per 100 ml. and fails to pass the A. S. T. M. copper strip corrosion test. If the phenol sulfide inhibitor is to be added to a fuel which satisfactorily passes the corrosion test but which nevertheless contains some unstable or reactive sulfur, it is likewise to be employed in the same limited quantity to obtain a satisfactory non-corrosive product.

Other additives for enhancing the qualities of the fuels may be admixed, such as oiliness agents, dyes, and pour point depressors. The Diesel fuels may contain viscosity modifiers, oxidation inhibitors, pour point depressants, and other ignition promoters. The gasoline type fuels may contain anti-knock agents, dyes, gum fluxes, anti-oxidants, etc.

The foregoing description and examples are intended to be illustrative only and not as limiting

invention is intended to be included within the scope of the claims.

I claim:

1. The method of inhibiting corrosiveness of a liquid hydrocarbon fuel stock of the gasoline to Diesel fuel boiling range normally corrosive to metals, which comprises adding to said fuel stock an effective corrosion inhibiting amount of an oil-soluble alkylated oxy-aryl sulfide in a range of about 0.001 to 0.05% by weight of said fuel stock.
2. The method of rendering a corrosive sulfur-containing fuel boiling between about 100° F. and about 700° F. non-corrosive to metals, which comprises adding to said fuel an oil-soluble alkyl phenol disulfide in an effective corrosion inhibiting amount of less than 0.05% by weight of said fuel.
3. The method of rendering a corrosive sulfur-containing fuel boiling between about 100° F. and about 700° F. non-corrosive to metals, which comprises adding to said fuel an alkyl phenol monosulfide in an effective corrosion inhibiting amount of 0.003% to 0.03% by weight of the fuel.
4. A liquid hydrocarbon fuel product of the gasoline to Diesel fuel boiling range normally corrosive to metals containing an oil-soluble alkylated oxy-aryl sulfide in an amount of 0.001% to 0.05% by weight of said liquid hydrocarbon product.
5. A compression-ignition engine fuel consisting essentially of a hydrocarbon Diesel fuel oil containing reactive sulfur components which are normally corrosive to copper and blended with an oil-soluble sulfide of an alkylated phenol in a corrosion inhibiting amount between the approximate limits of .003 to .03%.
6. A Diesel fuel consisting essentially of a hydrocarbon Diesel fuel base, from about 0.1% to about 5% of a sulfur-containing ignition promoter, and about 0.001% to 0.05% by weight of an alkylated phenol sulfide corrosion inhibitor.
7. A motor fuel consisting essentially of gasoline hydrocarbons and normally corrosive to copper, blended with a sulfide of an alkylated phenol in a corrosion inhibiting amount of less than 0.05% by weight of the fuel.
8. A liquid hydrocarbon fuel product of the gasoline to Diesel fuel boiling range normally corrosive to metals blended with from 3 to 20 milligrams of tertiary amyl phenol mono-sulfide per 100 milliliters, said fuel being satisfactorily non-corrosive to copper for one hour at 212° F. under the A. S. T. M. copper strip corrosion test.

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