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CORROSION INHIBITED GASOLINE

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2 Claims. (Cl. 44—63)

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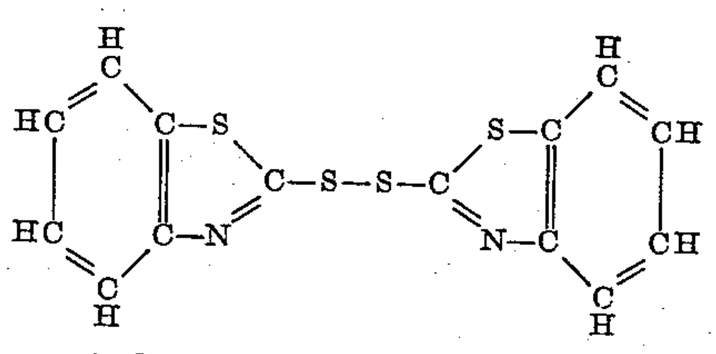
This invention relates to the inhibiting of corrosion of metals, particularly ferrous metals and copper, in contact with a light mineral hydrocarbon oil, such as gasoline.

One of the principal objects of the present invention is to provide a superior corrosion inhibitor for a light mineral hydrocarbon oil of this character, which can be effectively used in such extremely small quantities as not to affect the desirable properties and tests of the oil while at the same time effectively inhibiting corrosion of metal surfaces with which the oil comes in contact.

Other objects and advantages of the invention will be apparent from the following description and the appended claims.

The problem of internal corrosion of metal surfaces of vessels, pipes, containers, etc. used in the storage, transportation, handling and utilization of light hydrocarbon oils has long been recognized. With the increasing use of pipe lines to transport such finished petroleum products great distances, the problem has been accentuated. A high degree of refining of the light petroleum distillates has not been a complete solution of the problem, since this frequently involves more expensive processing with greater loss in yield than the ultimate utilization of the product justifies. Various inhibitors have been proposed for this purpose, and 2-mercapto benzothiazole has achieved substantial commercial use. While this inhibitor has proved quite satisfactory in most cases, it has been found not completely effective on certain highly corrosive light oil products such as those from high sulfur crudes; and, in other cases, objectionably large proportions of the inhibitor are required to effect the desired protection.

It has now been discovered that 2,2'-dibenzothiazol disulfide, which has the following structural formula



is unexpectedly superior as a corrosion inhibitor for light hydrocarbon oils. This material is a cream colored solid having a melting point of about 175° C., is soluble in benzene, chloroform and chlorobenzene and insoluble in water. Consequently, the inhibitor is not leached out when

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the light oil containing the same is stored in the presence of water. This inhibitor in powder form can be effectively applied to the light oil by forming a slurry of the same in a suitable hydrocarbon oil, such as a portion of the light oil to be inhibited, and then adding the slurry in controlled proportion. It has been found that this particular compound is unexpectedly more effective in certain more highly corrosive light oil distillates, and also has a high protective effect in gasolines which are to be transported through pipe lines, thereby enabling such a small proportion of the inhibitor to be employed as to have substantially no effect on the desirable properties and tests of the gasoline.

The commercial tests generally employed for determining the corrosion inhibiting effect of the inhibitor in light oils of this character are the copper strip corrosion tests at 122° F. and 212° F. respectively. In these tests, a sample of the petroleum oil is heated in contact with a copper strip at the stated temperature for a period of three hours. If any discoloration of the copper strip has occurred at the termination of the test, the same is reported as positive, meaning that the light oil is corrosive to copper under the conditions of the test. The discoloration will vary from a light red color for a mildly corrosive stock to a black color for a more highly corrosive oil. If no discoloration of the copper strip occurs, the test is reported as negative; and the sample is considered non-corrosive to metals under the conditions of the test. However, it has been found that certain light oils which are non-corrosive to copper in the test at 122° F. may result in objectionable corrosion when transported through pipe lines over long periods of time, or when used in certain metallic equipment where long service life is essential. For this reason, the more rigorous copper strip corrosion test at 212° F. is also employed as a measure of the effectiveness of the inhibitor in light oils to provide the required protection for such long service life.

The following results were obtained in comparative tests on a gasoline which show the superiority of 2,2'-dibenzothiazol disulfide as a corrosion inhibitor. A heavy straight run gasoline having a boiling range of 110°–410° F. obtained from a high sulfur crude was acid treated with 12 pounds per barrel of used alkylation acid (about 88% H_2SO_4) and then doctor sweetened. The resultant gasoline, after treatment, contained polysulfides; and motor fuel blends containing only a small proportion of this uninhibited stock were highly corrosive, producing a very

black copper cup when the standard copper dish gum test (a sample of the gasoline is evaporated to dryness in a freshly polished copper dish or cup) was made. Tests made on this treated corrosive stock by the copper dish gum test with and without the addition of the specified inhibitors in the indicated amounts gave the following results:

Table I

		2-mercapto benzothiazole			2,2'-dibenzothiazol disulfide		
Inhibitor #/M bbl	None	5	10	30	5	10	30
Copper dish gum	10	13	9	14	12	9	8
Copper dish corrosion	Pos.	Pos.	Pos.	Pos.	Pos.	Pos.	Pos.
	black	Peacock to black			Brown—much improvement		

In further explanation of the foregoing table, the copper cups from the samples inhibited with 2-mercapto benzothiazole were peacock colored around the upper rim which was only momentarily in contact with the corrosive sample, while by far the larger part of each cup was black. On the other hand, the copper cups from the samples inhibited with 2,2'-dibenzothiazol disulfide had no discoloration around the upper rim while the balance of each cup had only a brown discoloration indicating only slight corrosiveness by this rigorous test.

In order to show any possible adverse effect on the tests of a commercial motor gasoline, 2,2'-dibenzothiazol disulfide was added to one portion of the gasoline in an amount of 10 pounds per 1,000 barrels which was approximately five to ten times the dosage required to effectively inhibit this particular gasoline against pipe line corrosion. The following comparative tests were obtained on uninhibited and inhibited samples respectively of this test gasoline:

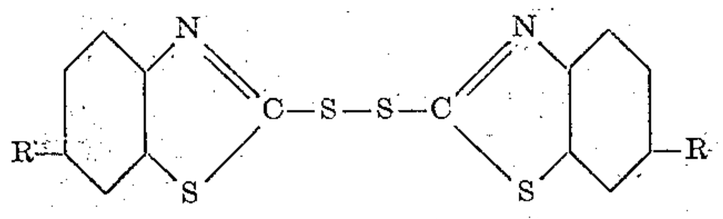
Table II

Test	Uninhibited Gasoline	Inhibited Gaseline
Gravity, °API	57.5	57.7.
Color	3" pink shade	3" pink shade.
Doctor Test	Negative	Negative.
Copper Strip Corrosion at 122° F	do	Do.
Read Vapor Pressure, #/sq. in	8.1	7.9.
Acid Heat	58	52.6.
Copper Dish Gum	10	10.
Glass Dish Gum	4 check 5	7 check 8.
ASTM Gum	2	2.
Lamp Sulfur	0.043	0.047.
10% Distillation, °F.:		
IBP	98	96.
5%	124	124.
10%	140	140.
20%	172	170.
30%	200	200.
40%	227	227.
50%	250	250.
60%	272	272.
70%	296	298.
80%	324	323.
90%	358	358.
95%	386	385.
E. P	408	408.
Per Cent Recovered	98.0	98.0.
Per Cent Residue	1.0	1.2.
Per Cent Loss	1.0	0.8.
Acidity of Distillation Residue.	Neutral	Neutral.
ASTM Octane	78.2	78.2.
CFRR Octane	84.9	85.1.

The foregoing data shows conclusively that the inhibitor of the present invention has no objectionable effect on the product quality of the motor fuel.

The 2,2'-dibenzothiazol disulfide can be effectively used as a corrosion inhibitor for the various gasolines in an amount within the range of about 0.5 to 10 pounds per 1,000 barrels (barrel of 42 gallons), depending on the corrosiveness of the particular base stock. Ordinarily, a proportion of about 1 pound per 1,000 barrels is sufficient for commercial motor fuel gasolines which are initially negative in the copper strip corrosion test at 122° F. in order to provide complete protection against pipe line corrosion. More highly corrosive gasolines will ordinarily be rendered effectively non-corrosive by the addition of around 3 to 10 pounds per 1,000 barrels, although somewhat smaller proportions are frequently satisfactory. The present invention enables untreated or highly corrosive light oil products to be effectively inhibited for satisfactory pipe line transportation, with a resultant substantial saving in treating cost as well as yield of product.

While the foregoing description discusses only the simple or unsubstituted 2,2'-dibenzothiazol disulfide, it is to be understood that the invention is not limited thereto but also includes derivatives formed by substituting organic groups for one or more of the hydrogen atoms on the benzene rings in 2,2'-dibenzothiazol disulfide. These are closely related compounds having the same basic structural formula which is believed responsible for the superior anti-corrosive properties. For example, one or more of the hydrogen atoms of the benzene rings in 2,2'-dibenzothiazol disulfide can be substituted by alkyl, aryl, aralkyl, alkaryl, heterocyclic, amino and other organic groups. Of particular interest in this connection are compounds having the structural formula:



where "R" is methyl, ethyl, propyl, butyl and larger alkyl groups to improve the oil solubility of the inhibitor while maintaining its effectiveness as an anti-corrosive. For convenience, the unsubstituted 2,2'-dibenzothiazol disulfide, as well as a derivative thereof as defined above, is generically termed in the following description and claims "a 2,2'-dibenzothiazol disulfide compound."

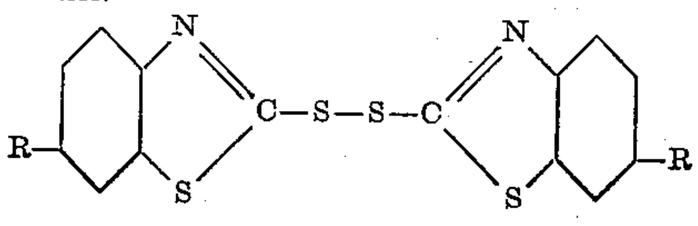
While 2,2'-dibenzothiazol disulfide has heretofore been suggested as an additive in substantially larger proportions for lubricating oil to impart extreme pressure properties and oxidation resistance to the lubricant, and also has been suggested as an additive in substantially larger proportions for a Diesel fuel heavier than gasoline to improve the stability and anti-corrosive properties thereof, it has not previously been suggested as an additive for gasoline. Consequently, its unexpected superiority over the mercaptoarylthiazole type of compound for this pur-

pose, particularly for corrosive gasolines from high sulfur crudes, had not been previously discovered. Moreover, its effective use in the extremely small proportion range of 0.5 to 10 pounds per thousand barrels, which does not alter the essential tests and properties of the gasoline while at the same time satisfactorily inhibiting corrosive attack of the gasoline on metal, is critically and unexpectedly different from the prior suggestions relating to the use of this disulfide type of compound in the heavier hydrocarbon oils.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A gasoline from a high sulfur crude and which is normally corrosive to metal, containing about 0.5 to 10 pounds per thousand barrels of a 2,2'-dibenzothiazol disulfide compound having the formula



where R is selected from the group consisting of hydrogen and alkyl, said small amount of the disulfide compound being effective to render said gasoline non-corrosive to metal while having substantially no effect on the desirable properties and tests of the gasoline.

2. A gasoline according to claim 1, where R of the formula for the disulfide compound is hydrogen.

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