July 12, 1966 G. S. GARDNER 3,260,538

METHOD OF INHIBITING CORROSION

Filed Nov. 26, 1963 3 Sheets-Sheet 1

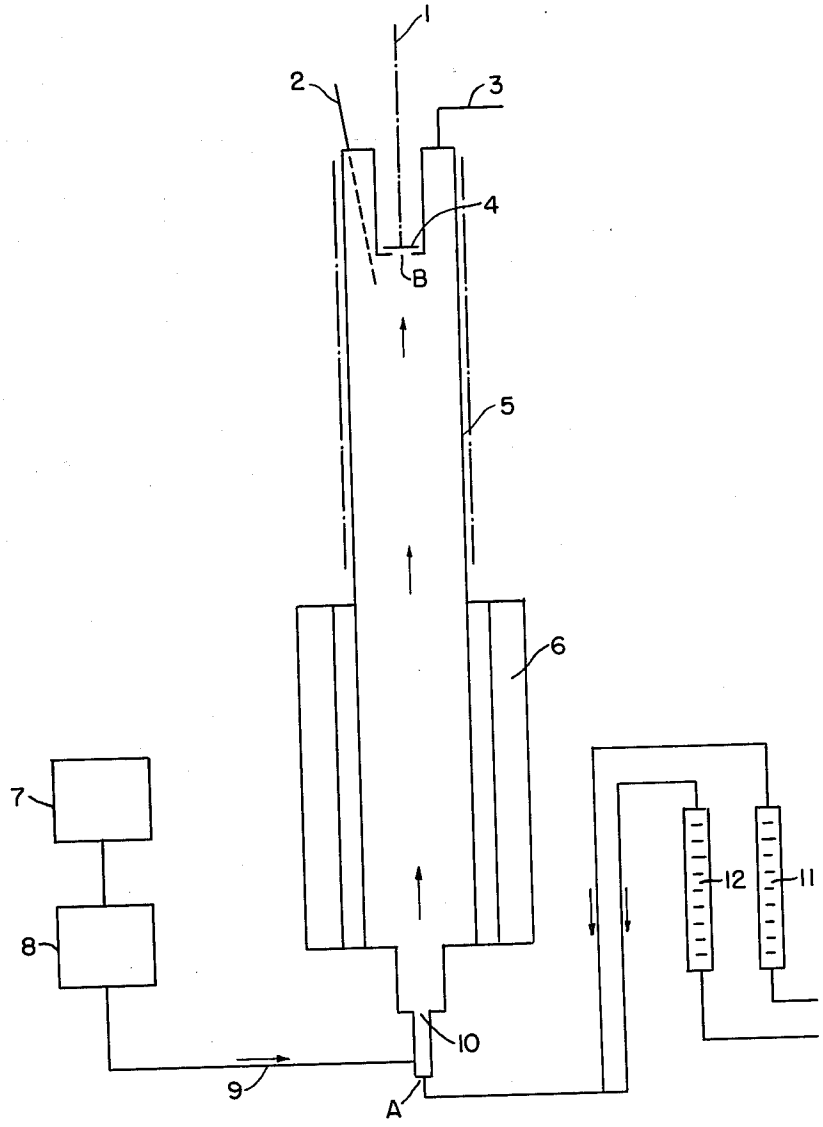

FIG. 1

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METHOD OF INHIBITING CORROSION

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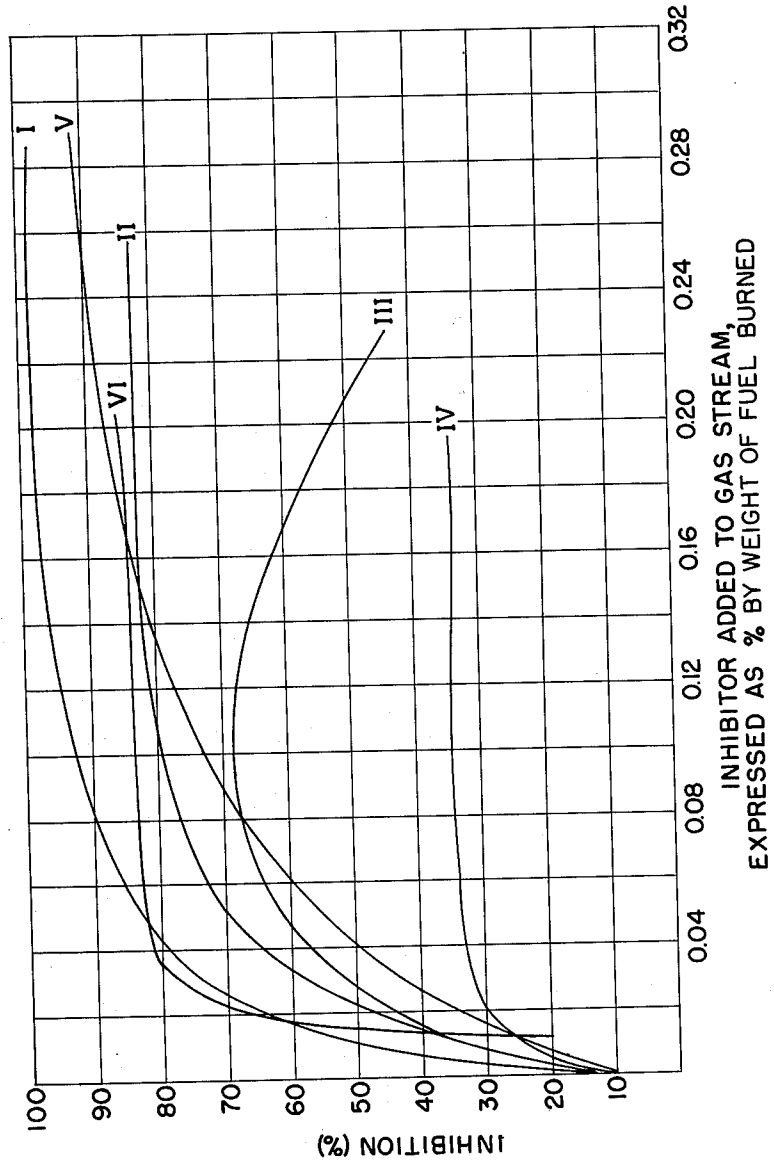

FIG. 2

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METHOD OF INHIBITING CORROSION

Filed Nov. 26, 1963 3 Sheets-Sheet 3

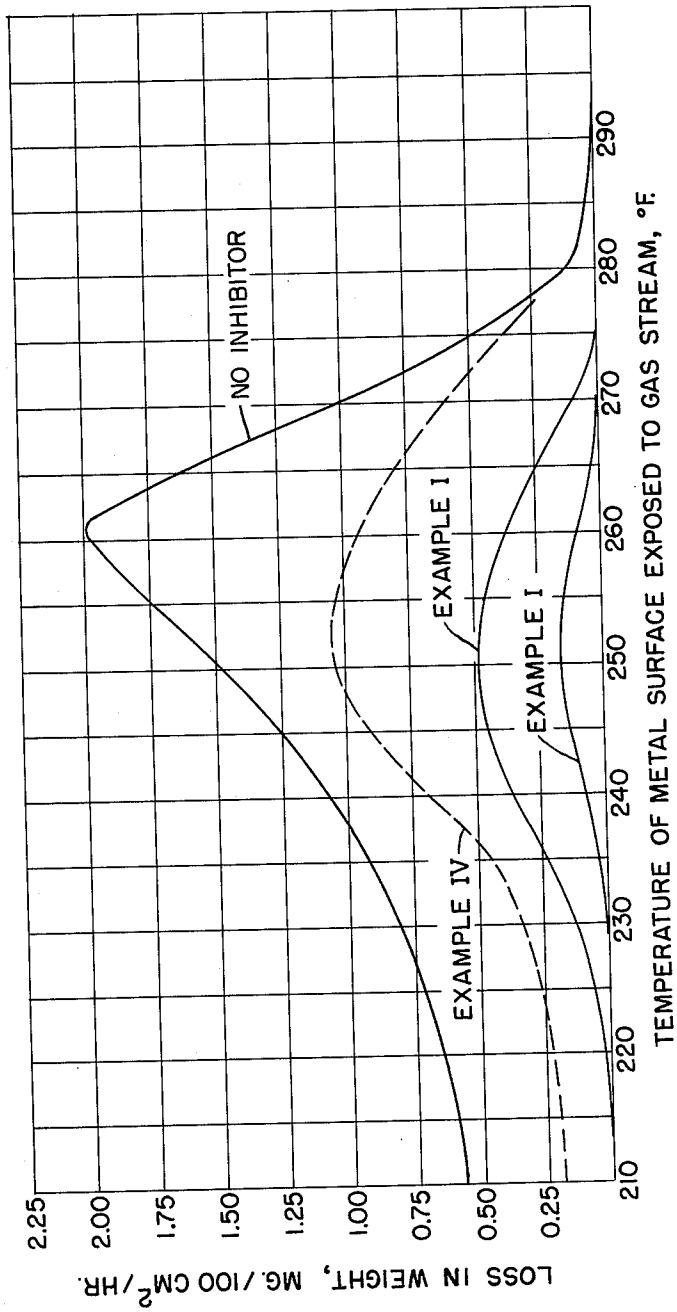

FIG. 3

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METHOD OF INHIBITING CORROSION

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2 Claims. (Cl. 252—391)

This invention relates to the art of reducing corrosion, and more particularly it relates to the reduction of corrosive attack on metal surfaces by acidic condensates resulting from the combustion of fuels.

The products of combustion of fuels, particularly industrial fuels, frequently contain highly corrosive components, primary among which are gaseous oxides of sulfur. These corrosive gases condense with moisture upon metal components in flue chambers and other members of industrial equipment, thereby giving rise to serious corrosion problems in turbines, air heaters, heat exchangers and the like.

In spite of the severity and widespread occurrence of this problem, not even a partial solution thereto existed until the appearance of the invention described in U.S. Patent 2,972,861. This patent teaches the use of tertiary amines, volatilized into the flue gas stream at a point outside of the combustion chamber, for purposes of retarding or preventing corrosive attack upon industrial equipment.

While these tertiary amine corrosion inhibitors, and the novel method of using them, sometimes impart a considerable measure of corrosion protection to metal surfaces, it has generally been found that where there is present in corrosive gases resulting from the combustion of industrial fuels, as much as 10 p.p.m. of sulfur trioxide (SO_3), corrosion inhibition may not exceed 35–40%, and at times may actually be as low as 25%, so that consistently reliable results are not always obtainable.

With the foregoing in mind, the principal object of the present invention resides in the provision of a method for reducing the corrosive attack of combustion gases upon metallic surfaces.

A further object of this invention is the provision of a method for reducing corrosive attack upon gas turbines, air heaters, heat exchangers and the like caused by acidic components in the products of fuel combustion gases.

How these objectives are obtained will now be described with reference to the accompanying drawings, wherein:

FIGURE I is a diagrammatic view of apparatus designed to reproduce field conditions simulating flue chambers for use in evaluating the improved corrosion inhibitor compositions of this invention.

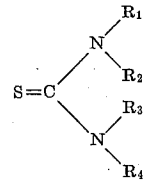
FIGURE II is a graph which illustrates improved corrosion inhibition obtained with this invention as compared to the use of prior art inhibitors.

FIGURE III is a graph which illustrates the effects of temperature upon corrosion inhibition and includes the effects of inhibitor compositions of this invention.

The present invention is based upon the surprising discovery that if there is injected into fuel combustion gases, at a point outside of the combustion chamber, an essentially non-volatile thiourea corrosion inhibitor in admixture with an amine corrosion inhibitor such as hereinafter defined, both of said corrosion inhibitors being dissolved or dispersed in or on a carrier which is volatile at the temperature of the flue gases, there will result a very high degree of corrosion protection of the metal components in contact with the flue gases even where the ratio of gaseous sulfur trioxide (SO_3) is high relative to the amount of gaseous sulfur dioxide (SO_2) present in these combustion products.

The precise theory responsible for the satisfactory operation of applicant's discovery is not known. While applicant does not wish to be bound by theory, it is believed that the non-volatile thiourea corrosion inhibitor, injected into the hot gaseous stream while it is dissolved in or dispersed upon a volatile carrier, is entrained by the hot gas stream, which rapidly volatilizes the carrier, and is carried thereby throughout the gas conduits and upon subsequent condensation of the acidic gases, is then entrapped in or on the condensate particles and is co-deposited therewith upon the metal surfaces. Suffice it to say that whatever theory is responsible for the operation of the applicant's process, it has been surprisingly discovered that greater than 80% reduction in corrosive attack, and at times greater than 90% corrosion inhibition can be obtained regardless of the SO_2/SO_3 ratio in the acidic, gaseous combustion products.

The thiourea corrosion inhibitors which have been found to be suitable for use in the process of this invention have the formula;



wherein R_1 and R_3 are selected from the group consisting essentially of hydrogen and alkyl groups containing from 1 to 3 carbon atoms, and wherein R_2 and R_4 are selected from the group consisting essentially of hydrogen, alkyl groups containing from 1 to 10 carbon atoms, and aryl and substituted aryl groups having from 6 to 10 carbon atoms.

Typical examples of the thiourea compounds which have been found to be suitable for use in this invention include:

Thiourea
1-methylthiourea
1,3-dimethylthiourea
1,1-dimethyl-3-ethylthiourea
1-methyl-3-isopropylthiourea
1,1-dimethyl-3-phenylthiourea
1-phenylthiourea
1-orthotolylthiourea
1,3-diorthotolythiourea
1-(B-naphthyl)-thiourea
1-isononylthiourea
1-stearylthiourea
1-olelylthiourea
1-methyl-3-dodecylthiourea
1,3-diethylthiourea
1,1,3,3-tetramethylthiourea
1,1,3-trimethyl-3-phenylthiourea

The amount of thiourea compounds which must be employed with the amine corrosion inhibitor in order to realize the surprising advantages of this invention has been found to be at least 5% of the total amount of com-

bined inhibitor utilized. If less than 5% of a thiourea compound is used, the resulting overall corrosion inhibition will be approximately the same as it would have been had amines been employed alone. Conversely, if more than 90% of thiourea compound is utilized, the amount of corrosion inhibition will not be of any appreciable significance since the amount of amine used will be too low for attainment of satisfactory results.

With respect to the amine corrosion inhibitor, this essential component may be selected from the group consisting essentially of tertiary amines and compounds containing a quaternary nitrogen atom. The tertiary amines include various organic nitrogen bases, such as the naturally occurring coal tar bases which are cyclic structures comprising at least one ring having both carbon and nitrogen atoms therein, and wherein the carbon atoms are saturated, such as pyridine and homologs thereof typical of which are the picolines, lutidines, collidines, piperidines, quinolines and acridines, as well as tertiary alkyl amines having from 1 to 10 total carbon atoms in each alkyl group. Preferred amines of this type are those having boiling points between 250 and 350° C.

Synthetic-organic nitrogen base corrision inhibitors which are also suitable for use in this invention include various substituted piperdines which are prepared by means of a modified Mannich reaction, and which are characterized in greater detail in U.S. Patent 2,807,585.

The compounds containing quaternary nitrogen atoms may be derived from the quaternization of any of the tertiary amines listed above. They also include the various commonly used corrosion inhibitors which contain a quaternary nitrogen atom such as for example, methylpyridinium chloride, dimethylpyridinium chloride, dissteraryldimethylammonium chloride, disoyadimethylammonium chloride, dicoco dimethylammonium chloride, as well as various other alkyl substituted trimethylammonium chlorides.

So far as concerns the amount of amine corrosion inhibitor which must be utilized in conjunction with the thiourea compound, it has been found that this must be at least 10% of the total amount of combined inhibitor utilized. Where the amount of amine used is less than 10% of the total inhibitor components, the resulting corrosion protection will be less than that which is commercially acceptable, and this is particularly true where the amount of sulfur trioxide is high as compared to the amount of sulfur dioxide which is present in the flue gas stream.

So far as the volatile carrier is concerned this may be water, a mineral acid, such as sulfuric or hydrochloric acids, or an organic solvent, such as a lower molecular weight alcohol or ketone. The important consideration with respect to the carrier is that it be volatile at the temperature of the gas stream when it is brought into contact therewith. It is not essential that the carrier be capable of solubilizing either the thiourea compound or the amine component since it has been found that dispersions of these corrosion inhibitors in the carrier perform equally as well as solutions thereof.

In order to obtain an acceptable rate of inhibition with the combined corrosion inhibitor of this invention, it has been found that at least 0.005% by weight of inhibitor, based upon the weight of fuel consumed should be used. Where less than this minimum amount is used, the corrosion results will be too poor to afford any worthwhile protection, and may, at times, be of a lower order than that which would have been obtained had only the amine component been employed. So far as the upper limit of total corrosion inhibitor is concerned, it has been found that there is no apparent limitation in this respect. However, a point of essentially maximum corrosion protection is reached when about 0.3% of inhibitor, based upon the weight of fuel consumed, is used, so that any inhibitor added in excess of this amount actually represents waste and such practice is undesirable from this viewpoint.

In order to illustrate the surprising features of this invention there are listed below several detailed examples which, however, are not intended to be construed as in any way limiting the scope of this invention.

Analysis of both industrial fuels, and the combustion products thereof have been made in order to determine the proper compositions of synthetic gaseous mixtures to be utilized in the corrosion tests. For example, residium oil utilized as fuel in industrial plants generally has an analysis approximately as follows:

Carbon	86%
Hydrogen	10%
Sulfur	4%

When one gram of such oil is burned with the theoretical amount of air properly to support combustion, there results about 12,000 cubic centimeters of gases measured at 77° F. and 760 mm. pressure, the analysis of which is about 90% N_2 and CO_2, and about 10% H_2O. Also included within these gases are about 2000 p.p.m. SO_2 and about 10 p.p.m. SO_3

In preparing synthetic gaseous admixtures for purposes of evaluating the corrosion inhibitor compositions of this invention, the inert nitrogen gas was replaced with CO_2, and the gas mixture was introduced into the apparatus at A, as is shown in FIG. I, at a rate of 7800 cc./minute (at 77° F. and 760 mm.). A hot-rolled, mild steel test specimen, from which scale had been removed by pickling in dilute, uninhibited hydrochloric at 77° F., followed by light sanding, was exposed at B in FIG. I for a period of time ranging from 3 to 24 hours. Evaluation of the effects of different corrosion inhibitor compositions of this invention was made against runs wherein no corrosion inhibitor was utilized, and where prior art practices were employed. Corrosion rates were calculated in terms of mg./100 cm.²/hour.

Example I

An admixture containing one part of diethylthiourea to 3 parts of mixed, high boiling pyridines and quinolines was added to a synthetic fuel combustion gas admixture having the analysis reported above. A hot-rolled, mild steel test specimen was inserted at point B of FIGURE I and, when the temperature of the metal surface had been heated to 250° F., the corrosive admixture of synthetic gases, along with the inhibitor, was permitted to impinge against the metal surface as is shown by the arrows in FIG. I. This test was continued for six hours, with the amount of corrosion inhibitor which was added being varied from 0.02 to 0.28% by weight based upon the theoretical fuel consumption which would provide, on burning, the same volume of gaseous components utilized. The results of this test are presented as curve I in FIGURE II, wherein the percent inhibition is plotted against the inhibitor as weight percent of fuel burned.

In each reported example a control run, conducted at the same temperature and utilizing the same type of metal test specimen, was made without benefit of any corrosion inhibitor. The purpose of these runs was the determination of corrosion loss for comparison with tests where there was used the corrosion inhibiting compositions of this invention. Percent inhibition, as reported in these examples was calculated by the formula:

$$\text{Percent inhibition} = \frac{\text{Corrosion loss without inhibitor} - \text{corrosion loss with inhibitor}}{\text{Corrosion loss without inhibitor}} \times 100$$

Example II

An admixture containing 1.25 parts of thiourea to each 4 parts of a piperidine compound prepared by the reaction of ammonium chloride, acetone and formalde-

hyde, such as described in Example A of U.S. Patent 2,807,585, was added to a mixture of gases typical of that which would be produced by the combustion of industrial fuel oil, and having an analysis corresponding to that reported above. This admixture of corrosive gases, containing from 0.02 to 0.28% by weight (based upon the weight of theoretical fuel consumption) of the corrosion inhibitor, was permitted to impinge against a metal test specimen, which had been heated to 250° F., for a period of six hours. The results of this test are shown in curve II of FIGURE II in comparison with results from other examples reported herein.

Example III

A quaternary ammonium corrosion inhibitor product was prepared by adding coal tar pyridine bases to dichloroethylether, heating these reactants, and adding thereto thiourea, such as is described in Example II of U.S. Patent 2,403,153. This product was then added to a mixture of gases, having an analysis corresponding to that given above, in an amount of from 0.02 to 0.28% by weight (based upon the weight of theoretical fuel consumption) and the admixture was permitted to impinge against a metal test specimen which had been heated to 250° F. The testing cycle was continued for 6 hours, and the corrosion results are presented as curve III in FIGURE II. Attention is called to the slope of this curve which drops off from a high of 68% corrosion inhibition at about 0.1% inhibitor (based on the weight of the fuel consumed) to 43% inhibition at about 0.23% inhibitor. This reduction in percent inhibition is attributed to the chloride ion level present in this particular inhibitor composition.

Example IV

Mixed tertiary amines of the pyridine types were added to synthetic gaseous admixtures such as used in Examples I to III, and having an analysis as reported above. The amines were added in amounts ranging from 0.02 to 0.28% by weight based upon the weight of the theoretical fuel consumption. The gaseous admixture was permitted to impinge against a metal test specimen maintained at 250° F. The entire testing cycle was continued for six hours. Results of this test, which are representative of prior art practice, are shown in curve IV of FIGURE II.

Example V

An admixture containing 100 parts of diethylthiourea to 11 parts of high boiling alkyl pyridines was added to a synthetic fuel combustion gas admixture, having the analysis reported above, over a range of from 0.02 to 0.28% by weight based upon the weight of the theoretical fuel consumption. This inhibitor admixture was permitted to impinge against a cold-rolled, mild steel test specimen inserted at point B of FIGURE II. The test cycle was continued for 6 hours at a temperature of 250° F., and results of the test are shown in curve V of FIGURE II.

Example VI

2.5 parts of diethylthiourea and 47.5 parts of alkyl pyridines were dissolved in isopropyl alcohol and this inhibitor solution was then added to a mixture of gases having an analysis corresponding to that given above in an amount varying from 0.02 to 0.28% by weight based upon the weight of the theoretical fuel consumption. This admixture was caused to impinge upon a clean, cold-rolled mild steel plate at 250° F. for 6 hours. Results of this test are shown in curve VI of FIGURE II.

Comparison of the results obtained from the six examples reported above, particularly as such results are demonstrated graphically in FIGURE II, demonstrates that corrosion inhibition ranging from upwards of 65% and even as high as 98% is obtained in accordance with the teachings of this invention when the amount of corrosion inhibitor employed ranges from about 0.02 to about 0.28% by weight, based upon the weight of the theoretical amount of fuel consumed, under the particular conditions of these tests. Conversely, where tertiary amines alone are used the percent inhibition rises initially to about 34% but then levels off notwithstanding further increases in the ratio of inhibitor to fuel.

Additional tests were conducted wherein the duration of the testing cycle was continued for either 6 or 22 hours at 250° F. with the amount of inhibitor being held constant over the testing cycle. These results, all of which utilized hot-rolled, mild steel as the test metal, are summarized below in Table I.

TABLE I.—INHIBITOR COMPOSITION

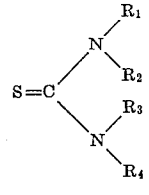
Tertiary amines, percent of total inhibitor	Thiourea, percent of total inhibitor	Amount of total inhibitor, percent of fuel	Time, hrs.	Percent inhibition
Control (none)	None	None	6	None
Mixed pyridines plus quinolines, 75.	Diethyl, 15	0.047	22	71
Mixed pyridines plus quinolines, 75.	do	0.093	22	93
Mixed pyridines, 40	1-methyl-3-dodecyl, 60.	0.15	22	68
Mixed tertiary alkyl amines (C_8–C_{10}), 15.	1-olelyl-, 85	0.20	22	80
Mixed tertiary alkyl amines (C_8–C_{10}), 15.	1-stearyl, 85	0.20	22	76
Mixed pyridine plus quinolines, 25.	1-phenyl, 75	0.15	22	73
Mixed tertiary alkyl amines (C_8–C_{10}), 75.	Thiourea, 25	0.10	22	82

From the above results it is apparent that the corrosion inhibiting process and compositions of this invention permits utilization of appreciably less inhibitor while simultaneously realizing far greater protection of the metal surfaces exposed to corrosive combustion gases than has heretofore been possible with the processes known in the art.

Attention is directed to the fact that the examples reported above utilized a temperature of 250° F. It has been found that elevated temperatures, particularly temperatures of 250° to 260° F. cause high rates of corrosion where no inhibitor is used or even where tertiary amines are used alone as the sole inhibitors. This discovery is illustrated on FIGURE III wherein it is seen that the inhibitor composition of this invention appreciably retards corrosion, even in the critical 250°–260° range.

I claim:

1. In the art of reducing fuel combustion gas acid corrosion of metals in a system where the metals are subjected to direct contact with combustion gases containing SO_3 produced by the firing of hydrocarbon fuels in a combustion chamber by introducing into the fuel combustion gases at a point outside of said chamber, but prior to contact with said metals, an amine corrosion inhibitor selected from the group consisting of tertiary amines and quaternary nitrogen compounds, the improvement which comprises adding to the amine inhibitor non-volatile thiourea corrosion inhibitor having the formula:



wherein R_1 and R_3 are selected from the group consisting of hydrogen and alkyl groups containing from 1 to 3 carbon atoms, and wherein R_2 and R_4 are selected from the group consisting of hydrogen, alkyl groups containing from 1 to 10 carbon atoms, and aryl and methyl substituted aryl groups having from 6 to 10 carbon atoms, the amount of said thiourea being from 5 to 90% of the total amount of combined inhibitor, both of said inhibitors being present in an amount of at least 0.005% by weight based upon the weight of the fuel oil consumed, and dissolved or dispersed on a liquid carrier which is volatile at the temperature of the flue gases.

2. The method of claim 1 wherein the thiourea compound is 1,3-diethylthiourea.

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