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TREATMENT OF HYDROCARBON OILS

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This invention relates to a means of preventing corrosion of metals in contact with hydrocarbon oils and more particularly to imparting non-corrosive properties to hydrocarbon oils.

Internal corrosion of vessels used in the transportation and storage of hydrocarbon oils is frequently severe. The extent or rate of corrosion varies markedly with the type of service and the corrosive constituents present with the oil. Such factors as velocity of flow of the hydrocarbon oil over the metal surface, temperature, and clarity of the oil in some cases have marked effects on the corrosion rate. Corrosion frequently results from the action of sulfur, oxygen, or compounds of these elements, since examination of many specimens of iron pipe from various sources showed the presence of iron sulfide or iron oxide as corrosion products on the inner surface of the pipe. The corrosion products on the surface of the metal frequently lead to localized corrosion with resultant pitting and failure, although occasionally they serve to inhibit further action.

The corrosion of tanks, pipes and the like results in great economic loss. The corrosion of metals in contact with hydrocarbons is in addition objectionable in that the internal condition of a vessel, for example a pipe, cannot readily be determined, so that hazardous conditions may develop without being evident. In some uses, such as pipe lines transporting gasoline, internal corrosion seriously decreases the volume of liquid which will flow under constant pressure, necessitating extensive cleaning operations. A satisfactory elimination of corrosion through removal of corrosive constituents is frequently not possible. Eliminating this internal corrosion results in increased satisfactory operation and life of hydrocarbon oil containers.

An object of the present invention is to produce a hydrocarbon oil composition, through addition of inhibitors to that oil, which imparts corrosion resistance to metals with which it is in contact.

A further object of this invention is to substantially prevent the internal corrosion of metal pipes, tanks and other containers, particularly of iron and copper compositions, used in the transportation and storage of oil, gasolines, liquefied petroleum gases and the like, through addition of corrosion inhibiting compounds to those hydrocarbon liquids.

The special composition of corrosion-inhibiting oil herein disclosed is adaptable for use in process tanks, pumps, baths, and the like, wherein a diminution of corrosion in hydrocarbon-containing vessels is desired.

According to the present invention, through incorporation in a hydrocarbon oil or fraction, cut or product derived therefrom, of a small amount of suitable material, corrosion of metals in contact with the oil is markedly diminished.

The compounds which have been found to possess the desirable qualities set forth, in that a small portion thereof when incorporated in a hydrocarbon oil mixture materially decreases the rate of attack of the containing vessel, are the aryl thiazoles, or more particularly the mercapto aryl thiazoles.

We believe the inhibition of corrosion results from the formation of a practically impervious film or coating on the surface of the metal through contact of the mercapto aryl thiazoles with metal, especially iron and copper compositions. The film thus formed serves to prevent or impede access of the corroding agents to the metal, thus inhibiting corrosion.

The following example illustrates the use of mercapto benzo thiazole in diminishing the corrosion of iron. A representative finished refinery gasoline was found to be corroding a pipe line through which it was passing. Small streams of this commercial gasoline, to some of which had been added mercapto benzo thiazole, were passed over test bars of iron composition the same as that of the pipe line for a period of sixty days. At the end of the test period, the bars were examined. The results are given in the adjoining table.

Weight per cent mercapto benzo thiazole	Observations
0.0030	No corrosion
0.0007	Slight spotting
No inhibitor	Surface rusted

In addition to diminishing the rate of attack of uncorroded surfaces, mercapto aryl thiazoles possess the further advantage of effectively stopping corrosion after the metal surface is already rusted. The corrosion products are loosened, allowing penetration of the inhibitor directly to the uncorroded metal. This property is especially valuable in the case of localized corrosion resulting in pitting and barnacle growth. The increase of resistance to flow resulting from corrosion is diminished through such treatment.

One of the commercial tests for finished petroleum fuels, gasolines and the like is to heat the petroleum oil in contact with a copper strip

at a stated temperature for a definite period, for example at 122° F. for three hours. It is difficult to treat certain petroleum oils so that they satisfy this test. Addition of quantities of mercapto benzo thiazole approximating 0.002 weight per cent to the oil inhibits discoloration of the copper in the corrosion test.

Various of the substituted aryl thiazoles, such as mercapto tolyl thiazole, mercapto xylyl thiazole, and mercapto 5 ethyl benzo thiazole have been found to be effective as corrosion inhibitors for the purposes enumerated above. Other groups, such as alkyl, amino, hydroxyl or halogen substituted in the benzene ring, are useful in altering the solubility and activity of the thiazole in hydrocarbon oils.

The quantity of inhibitor used is dependent upon the extent to which it is desired corrosion be eliminated, the severity of corrosion encountered, the amounts and kinds of materials found in the hydrocarbon mixtures, the temperature, and to some extent on the amount of corrosion which has already occurred. Quantities of inhibitor, for example mercapto benzo thiazole, in amounts within the range 0.01 to 0.0001 weight per cent are preferably employed. However, in certain uses quantities as high as 0.1 weight per cent, or hydrocarbon oils saturated with inhibitor, are desirable; in other uses quantities of inhibitor less than 0.0001 weight per cent are found to exert a beneficial effect.

Since the mercapto aryl thiazoles are solids at normal temperatures, they may be added batchwise or continuously to hydrocarbon oils in a variety of ways. For example, the compound may be added in the form of a powder directly to the gasoline, or an equally satisfactory and in some cases more convenient method is that of mixing the powdered inhibitor with a viscous oil to form a slurry or paste, which may be added to the hydrocarbon oil. If desired, the inhibitor may be dissolved in a solvent such as benzene or alcohol, fully miscible with the hydrocarbon oil, and this concentrated solution of inhibitor added in desired amounts to said oil. This method is especially useful in adding small known quantities of inhibitor.

Since still other modes of employing the various inhibitors of the class hereinbefore set forth in the protection of metals in contact with hydrocarbon oils may be apparent to those skilled in the art to which this invention pertains, the present invention is limited solely by the claims attached hereto.

What is claimed is:

1. The method of inhibiting the corrosion of corrodible metals when contacted with light liquid hydrocarbons containing constituents normally corrosive to said metals which comprises adding to the said liquid hydrocarbons a small amount of a mercapto aryl thiazole.

2. The method of inhibiting the corrosion of corrodible metals when contacted with light liquid hydrocarbons containing constituents normally corrosive to said metals which comprises adding to the said liquid hydrocarbons a mercapto benzothiazole in an amount within the range of 0.01 to 0.0001 per cent by weight of said liquid hydrocarbon.

3. A light liquid hydrocarbon to which has been added as a corrosion inhibitor a small amount of a mercapto aryl thiazole.

4. A light liquid hydrocarbon to which has been added as a corrosion inhibitor a small amount of a mercapto benzothiazole.

5. The method of inhibiting the corrosion of corrodible metals when contacted with light liquid hydrocarbons containing constituents normally corrosive to said metals which comprises adding to the said liquid hydrocarbons a mercapto tolyl thiazole in an amount within the range of 0.01 to 0.0001 per cent by weight of said liquid hydrocarbon.

6. The method of inhibiting the corrosion of corrodible metals when contacted with light liquid hydrocarbons containing constituents normally corrosive to said metals which comprises adding to the said liquid hydrocarbons a mercapto-5-ethyl-benzo-thiazole.

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