United States Patent Office 2,768,884 Patented Oct. 30, 1956

2,768,884

CORROSION PREVENTION

Rolland G. Bowers, Toledo, Ohio, assignor to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

No Drawing. Application November 12, 1952, Serial No. 320,117

9 Claims. (Cl. 44—73)

This invention relates to the prevention of corrosion in pipe lines employed for the transmission of hydrocarbon oils and particularly for the transmission of hydrocarbon oils boiling in the range of from 300° F. to 700° F.

In the transmission of hydrocarbon oils through ferrous pipe lines over long distances considerable trouble has been encountered with corrosion. This difficulty is usually attributed to the presence of water entrained or dissolved in the hydrocarbon oil, or to naturally occurring corrosive materials such as sulfur compounds. The presence of metal compounds, such as copper and iron compounds which may be dissolved or suspended in the oil, accelerates the corrosion of pipe lines transmitting the oil. A further difficulty is the formation of gum and sediment of an asphaltic nature in the hydrocarbon oil during transmission. The control of corrosion, gum formation and sediment formation is important, because the formation of iron oxide, gum or sediment decreases the capacity of the pipe line and hence decreases the volume of liquid which will flow under a given pressure. Furthermore, rust may slough off, be carried with the oil, and accumulate at some point in the transmission system to stop effectively the flow of oil. Gum or sediment may also effectively stop the flow of oil in a similar manner.

It has been proposed to add various substances to hydrocarbon oils to prevent corrosion of contacting metal surfaces. Such additions, however, have not been completely satisfactory. While such added materials may exhibit corrosion-inhibiting properties, acceleration of deleterious effects, such as gum or sediment formation may simultaneously be observed. Similarly, materials heretofore proposed as gum inhibitors suffer one or more difficulties as above described, e. g., the acceleration of deleterious effects or contamination of the oil. A further difficulty is that materials added to certain hydrocarbon fractions, such as gasoline fractions, to achieve a desired result do not appear effective to give such a result when employed with higher boiling fractions, such as furnace oils or diesel fuels.

An object of the present invention is to provide a method for the transmission through ferrous conduits such as pipe lines of hydrocarbon oils boiling in the range of from 300° F. to 700° F. which substantially obviates corrosion difficulties. A further object is to provide a method for preventing corrosion of pipe lines transmitting hydrocarbon oils and for simultaneously inhibiting gum formation and the formation of similar materials as sediment in hydrocarbon oils during such transmission. Other objects will be apparent from the following specification.

It has now been found that by incorporating corrosion-inhibiting quantities of an aliphatic secondary amine and a diaminopropane, as hereinafter defined, in a hydrocarbon oil boiling in the range of from 300° F. to 700° F., the corrosion of pipe lines through which the resulting composition is transmitted is effectively prevented, and

gum and sediment formation during such transmission is simultaneously inhibited. Thus, by adding small quantities of two materials, both of which are soluble in the hydrocarbon oil at least in their effective concentrations, as hereinafter defined, the above and other objects are achieved.

The aliphatic secondary amines which may be employed have two aliphatic groups and one hydrogen atom attached to a nitrogen atom, and each aliphatic group has at least 2 and not more than 20 carbon atoms. It is preferred to employ an amine having a total of not more than 30 carbon atoms. To illustrate the aliphatic secondary amines which may be employed, diethylamine, dipropylamine, ethylpropylamine, diisopropylamine, dibutylamine, diamylamine, diisoamylamine, and the hexyl-, heptyl-, octyl-, nonyl-, and decyl-amine homologues thereof give good results.

The diaminopropane to employ is N:N'-disalicyclidene-1,2-diaminopropane, and it does not appear that other materials may be substituted therefor for use in connection with aliphatic secondary amines in the process of the present invention.

The quantity of aliphatic secondary amine to employ may be varied from 0.00001 to 0.05% by weight of the hydrocarbon oil, but preferably is manitained within the range of from 0.001 to 0.02% by weight. The quantity of the diaminopropane to employ may be varied from 0.00001 to 0.05% by weight of the hydrocarbon oil, but preferably is maintained within the range of from 0.0001 to 0.02% by weight. For example, using the preferred amine, dibutylamine, 0.005% by weight thereof with 0.001% by weight of the diaminopropane gives excellent results. The amine and diaminopropane are added to the hydrocarbon oil prior to its transmission through pipe lines and the addition may be made at any time subsequent to the preparation of the oil and prior to its transmission through a pipe line. After the addition of the two components to the oil, corrosion of contacting metal surfaces, such as metal containers, and gum and sediment formation in the oil are not observed to any substantial extent, and hence it is advantageous to add the components as soon as feasible after the preparation of the oil. In this manner, corrosion and gum formation are controlled throughout storage and transmission and thereafter until the oil is consumed. It is therefore apparent that an object achieved by the present invention is the prevention of corrosion to metal containers and the inhibition of gum and sediment formation in the oil during storage, although these storage problems are not as serious as when the hydrocarbon oil is being subjected to transmission through a pipe line for a relatively long distance.

As above stated, both the aliphatic secondary amine and the diaminopropane are soluble in hydrocarbon oils within their operative concentration range, and hence the use of aqueous solutions of inhibitors, as heretofore proposed, is unnecessary. In some instances, however, the injection of small amounts of an aqueous solution of sodium chromate into a pipe line during oil transmission gives a beneficial effect, and such operation may be employed in the present process if desired.

It has been observed that after transmission of a furnace oil or a diesel fuel containing an aliphatic secondary amine and the diaminopropane, as above defined, the pipe line is effectively protected against corrosion for a substantial time during subsequent transmission of the same or other hydrocarbon fractions not containing an aliphatic secondary amine or an aminopropane as herein described. For example, after passing a quantity of furnace oil containing the subject additives, a gasoline fraction uninhibited against corrosion and which would normally cause corrosion may be passed through the

pipe line without attack on the metal pipe. Accordingly, a preferred embodiment of the process of the present invention is the alternate transmission of a furnace oil or a diesel fuel containing an aliphatic secondary amine and a diaminopropane, as herein described, and the transmission through the same pipe line of the same or a different hydrocarbon oil without the added materials.

The following examples illustrate embodiments of the invention:

Example 1

To illustrate the process of the present invention, a No. 2 furnace oil having a boiling range of from 350° F. to 650° F. and a Saybolt Universal viscosity of about 35 (at 100° F.) was transmitted through a subsurface pipe line about 60 miles long. An aqueous solution containing 10% sodium chromate was injected at a rate so that 1 pound of sodium chromate per 1000 barrels of oil pumped was added. It was frequently necessary to scrape the interior of the pipe to remove rust and gum, and considerable quantities thereof were removed by such scraping. Scraping was necessary at intervals of about 1 month in order to maintain efficient operation. To the same furnace oil was added 0.005% by weight of dibutylamine and 0.001% by weight of N:N'-disalicyclidene-1,2-diaminopropane and the resulting composition was transmitted by the same operation through the same pipe line. It was found that corrosion was very greatly reduced and no difficulties with gum or sediment formation were observed after long operation. In order to prove this effect, the oil was tested by transmission through the pipe line for 2 years, and during this time no difficulties with corrosion, gum or sediment were experienced. Scraping of the pipe at the same intervals as above stated resulted in the removal of much less rust, gum and sediment, thus showing that scraping could be performed at substantially greater intervals, if not entirely dispensed with.

Substantially identical results are obtained when diesel fuel or No. 1 furnace oil is submitted for No. 2 furnace oil.

Example 2

To illustrate the effect of using both the aliphatic amine and diaminopropane, three different No. 2 furnace oils from various sources and designated oil A, B and C were subjected to an accelerated test by heating to 190° F. for 10 days and gum formation, as exhibited by sediment, was determined. To oils B and C were added 0.1 part per million of copper and iron in the form of naphthenates. For comparison, oil A was tested without the addition of any material, and all oils were tested using N:N'-disalicyclidene-1,2-diaminopropane alone, dibutylamine alone, and the combination thereof, as shown in the table.

The following results were obtained, in which sediment is recorded as milligrams per 100 milliliters of oil.

	No additive	0.001 wt. percent of diaminopropane	0.005 wt. percent of dibutylamine	0.001 wt. percent diaminopropane + 0.005 wt. percent dibutylamine
Oil A	13.4	4.5	0.8	0.5
Oil B		2.4	5.2	1.8
Oil C		1.2	5.8	0.8

These data show that a substantial reduction in sediment is obtained using the diaminopropane and dibutylamine in combination as compared to the reduction obtained when either additive is used alone.

Example 3

To further demonstrate the process of the present invention, No. 2 furnace oil and the same oil containing both 0.001 wt. percent of N:N'-disalicyclidene-1,2-diaminopropane and 0.005 wt. percent of dibutylamine were periodically delivered to three similar storage tanks of 275 or 300 gallons capacity over a period of about 6 months. The following data on rust and sediment were obtained, "Uninhibited" meaning the oil without additives (tank #1) and "Inhibited" meaning the oil containing the specified additives (tanks #2 and 3):

	Uninhibited (Tank #1)	Inhibited (Tank #2)	Inhibited (Tank #3)
Total oil delivered (gallons)	1,311	1,172	951
Residual oil in tank at time of test (gallons)	70	120	70
Sediment in residual oil (mg./100 ml.)	10.7	4.4	1.7
Rust in residual oil (mg./100 ml.)	35.6	2.2	0.2

These data show a substantial reduction in sediment and rust in accordance with the process of the present invention.

Example 4

Various aliphatic secondary amines were employed, together with N:N'-disalicyclidene-1,2-diaminopropane, in the process of the invention using No. 2 furnace oil. The resulting compositions were aged 10 days at 190° F. in contact with metallic iron, which conditions are much more drastic than encountered in normal use of the oil. Total gum content was determined by an acid flocculation method which determines the total gum content including unfilterable colloidal gum (Proell and Bolt, Oil and Gas Journal, 234–5 (1946). Sediment was determined on the same samples by filtering a uniform sample, drying and weighing. For comparison, data obtained on the same oil with no added materials are included.

Amine added	Quantity of Amine (Wt. Percent)	Quantity of Diaminopropane (Wt. Percent)	Gum Content (mg./100 ml.) No additive	Gum Content (mg./100 ml.) With additives	Sediment (mg./100 ml.) No additive	Sediment (mg./100 ml.) With additives
dibutylamine	0.005	0.002	26	17	6.1	0.9
Do	0.01	0.002	26	17	6.1	0.7
diamylamine	0.005	0.002	26	17	6.1	1.0
Do	0.01	0.002	26	16	6.1	0.9
diisopropylamine	0.007	0.001	42	22	9.5	1.9
dibutylamine	0.005	0.001	42	21	9.5	0.9
Do	0.007	0.001	42	16	9.5	1.5
diamylamine	0.007	0.001	42	19	9.5	1.4
diisoamylamine	0.007	0.001	42	18	9.5	1.1
dihexylamine	0.007	0.001	42	19	9.5	1.0

The foregoing examples illustrate embodiments of the process of the present invention. When other secondary aliphatic amines are employed within the limits herein defined similar results are obtained.

I claim:

1. Method of controlling corrosion of ferrous metal surfaces of conduits and reducing gum formation during transmission of a hydrocarbon oil boiling in the range of from 300° F. to 700° F. which comprises transmitting through the conduit said oil in which has been incorporated corrosion-inhibiting quantities of N:N'-disalicylidene-1,2-diaminopropane and an aliphatic secondary amine selected from the group consisting of diisopropylamine, dibutylamine, diamylamine, diisoamylamine and dihexylamine.

2. Method according to claim 1 wherein said aliphatic secondary amine is dibutylamine.

3. Method according to claim 1 wherein said aliphatic secondary amine is diamylamine.

4. Method according to claim 1 wherein said aliphatic secondary amine is diisoamylamine.

5. Method according to claim 1 wherein said aliphatic secondary amine is dihexylamine.

6. Method according to claim 1 wherein said aliphatic secondary amine is diisopropylamine.

7. Method of controlling corrosion of ferrous metal surfaces of conduits and reducing gum formation during transmission of a hydrocarbon oil boiling in the range of from 300° F. to 700° F. which comprises transmitting through the conduit said oil in which has been incorporated corrosion-inhibiting quantities of N:N' - disalicylidene - 1,2 - diaminopropane and an aliphatic secondary amine having from 3 to 6 carbon atoms in each alkyl group.

8. Method of controlling corrosion of ferrous metal surfaces of conduits and reducing gum formation during transmission of a hydrocarbon oil boiling in the range of from 300° F. to 700° F. which comprises transmitting through the conduit said oil in which has been incorporated from 0.00001 to 0.05% by weight of N:N'-disalicyclidene - 1,2 - diaminopropane and from 0.00001 to 0.05% of an aliphatic secondary amine having from 3 to 6 carbon atoms in each aliphatic group.

9. Method of controlling the internal corrosion of a ferrous metal pipe during transmission of hydrocarbon oils which comprises transmitting through said pipe line a hydrocarbon oil boiling in the range of from 300° F. to 700° F. having incorporated therein corrosion-inhibiting quantities of N:N' - disalicyclidene - 1,2 - diaminopropane and an aliphatic secondary amine having from 3 to 6 carbon atoms in each aliphatic group, discontinuing transmission of said hydrocarbon oil, and thereafter transmitting through said pipe line a hydrocarbon oil uninhibited against corrosion, whereby corrosion of said pipe is substantially prevented.

References Cited in the file of this patent

UNITED STATES PATENTS

2,369,490	Proell	Feb. 13, 1945
2,473,455	Sorg	June 14, 1949
2,560,633	Stedman	July 17, 1951
2,626,208	Brown	Jan. 20, 1953
2,641,539	Thompson et al.	June 9, 1953