

UNITED STATES PATENT OFFICE

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PREVENTION OF RUST

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My invention is concerned with the maintenance of product pipe lines and storage vessels and more particularly pertains to a method for preventing internal corrosion of equipment of this type when constructed of steel or other iron-containing metal. The invention is especially valuable as applied to gasoline pipe lines but is also applicable to pipe lines employed in the transportation of other petroleum oil distillates as kerosene or fuel oil, for example.

Internal corrosion of product pipe lines is undesirable, inter alia, because of the contamination of distillate with corrosion products and because the consequent restriction of the internal diameter of the pipe decreases the volume of distillate which can be transported therethrough over a given period under a constant pressure.

I have made the surprising discovery that the incorporation in light petroleum distillates of minute amounts of mahogany sulfonic acids or sulfonates materially retards internal corrosion and scale formation in pipe lines used for the transportation of such distillates. By "minute amounts" I refer to concentrations of the order of 1 to 100 parts per million.

Because of the presence of both free oxygen and water in gasoline as normally produced, pipe lines employed in transporting gasoline are particularly prone to corrode. During treating operations or storage it is not uncommon for as much as .006% of oxygen to become dissolved in gasoline. Water, picked up as from a washing operation, may be present as entrained water or as dissolved water. In any event, it is normally present in such amounts that the inner pipe wall is maintained in a wet or moistened condition at all times. Corrosion, of course, is accelerated by the normally rapid flow of gasoline through pipe lines.

In the practice of my invention, I generally use mahogany sulfonates rather than the corresponding sulfonic acids but the latter are applicable as previously indicated. The sulfonic acids and sulfonates may be typified by the formula RSO_3X , in which R represents hydrocarbon radicals derived from petroleum and X

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may be hydrogen, a metal, or an amine radical having a molecular weight not exceeding 150.

I have obtained best results with the amine sulfonates and, accordingly, I prefer these over the metal sulfonates. One advantage of the amine sulfonates, apart from their greater effectiveness in the respect of corrosion inhibition, is that they leave no residue on burning or combustion of the fuel.

The mahogany sulfonates are prepared directly or indirectly from sulfuric acid-treated oil. Ordinarily, the alkali and alkaline earth metal sulfonates are produced by reacting the acid oil, from mineral white oil manufacture for example, with the hydroxide of the metal or with the oxide in the presence of water. Other metal sulfonates, as the cadmium and manganese sulfonates, are most expeditiously produced, meta-thetically, by reaction of appropriate salts of the metals, e. g. $CdCl_2$, $MnSO_4$, with the sodium sulfonate, while still others are obtained most readily by reacting a theoretical excess of the acetate of the metal with the acid oil. In some instances, notably aluminum, the sulfonate can be prepared by direct reaction of the metal and acid oil.

Ordinarily, I obtain the amine sulfonates by reacting the amine and acid oil directly, using the amine in substantially theoretically required proportions as determined by the acid number of the oil. In most cases heat is evolved. Where the solution of the product sulfonate is not clear, it may generally be rendered so by heating to a temperature of the order of 150-180° F. The amine sulfonates which settle out of the reaction mixture can usually be solubilized by dilution with an amount of kerosene equal to the volume of oil present. In some instances, the addition of a small amount of water, as 5% on the weight of the reaction mixture, and the use of temperatures upwards of 260° F. are necessary to achieve reaction between the amine and acid oil. This is required in the case of alpha naphthylamine sulfonate, for example.

In Table I below are given properties of amine sulfonate products I have prepared and tested.

Table I

	Percent Nitrogen	Theoretical Percent Nitrogen	Percent of Theoretical Amine Used	Description
Aniline sulfonate.....	0.39	0.33	100	10% sulfonate in oil; slightly hazy.
Butylamine sulfonate.....	0.33	0.33	115	10% sulfonate in oil; light and clear.
Diethylamine sulfonate.....	0.30	0.33	115	10% sulfonate in oil; light and clear.
Dimethyl-aniline sulfonate.....	0.37	0.32	100	10% sulfonate in oil. ¹
Ethanolamine sulfonate.....	2.12	² 2.77	115	76% sulfonate in oil.
Ethylamine sulfonate.....	0.30	0.33	115	10% sulfonate in oil; light and clear.
Ethylenediamine sulfonate.....	2.7	² 6.6	100	41% sulfonate in oil.
Alpha-naphthylamine sulfonate.....	0.37	0.32	100	10% sulfonate in oil; dark red color.
Piperidine sulfonate.....	⁴ 0.15	0.33	115	10% sulfonate in oil; light and clear.
Pyridine sulfonate.....	⁴ 0.08	³ 0.16	100	5% sulfonate in oil and kerosene.
Triethanolamine sulfonate.....	0.56	³ 2.36	115	24% sulfonate in oil; hazy.

¹ Tested as 5% concentrate in oil and kerosene.

² Calculated for an oil free sulfonate.

³ Calculated for a concentrate containing 5% sulfonate.

⁴ Kjeldahl nitrogen determinations are not quantitative for pyridine derivatives.

Metal sulfonates I have prepared and tested include aluminum sulfonate, cadmium sulfonate, calcium sulfonate, copper sulfonate, ferric sulfonate, lead sulfonate, nickel sulfonate, sodium sulfonate and zinc sulfonate.

I have found it advantageous to incorporate the sulfonate in the distillate as an oil concentrate containing about 10% of the sulfonate. Where the sulfonate is insoluble or incompletely soluble in the oil component of the acid oil from which it was derived, alcohol or benzene, for example, may be added in sufficient amounts to bring all of it into solution.

The suitability of the mahogany sulfonic acids and sulfonates as pipe line rust inhibitors is demonstrated by subjecting blends containing the sulfonic acids or sulfonates to a test analogous to that carrying ASTM designation D-665-42T. According to my modified test, a polished mild steel strip is suspended in a beaker fitted with a mechanical stirrer and containing 350 mls. of the test blend. The blend is stirred for 30 minutes after which 50 mls. thereof are removed and 30 mls. of distilled water substituted. Stirring is continued for 48 hours or longer and the strip then inspected for rust.

The appended table compares the effectiveness of various additives within the scope of my invention in such test. In the experiments of the table kerosene was employed as the inhibited distillate because it is less volatile than gasoline.

Table II

Additive	Additive Conc., lbs./1,000 bbls. (expressed as total amount conc. containing 10% dry soap)	Molecular Weight of Amine	Rust Rating ¹
Blank			Completely rusted.
Mahogany sulfonic acids	18		B++ ²
Do.	25		B++ ²
Aniline sulfonate	25	93	B+
Do.	100	93	A
Butylamine sulfonate	25	73	B+
Do.	38	73	B+
Diethylamine sulfonate	25	73	B++
Do.	38	73	A
Dimethyl aniline sulfonate	25	121	A ²
Ethanolamine sulfonate	18	61	B
Ethylamine sulfonate	25	45	B
Do.	36	45	B++
Ethylene diamine sulfonate	25	60	B
Alpha-naphthylamine sulfonate	25	143	B++ ²
Piperidine sulfonate	25	85	B+
Pyridine sulfonate	25	79	B++
Triethanolamine sulfonate	12	149	B+
Aluminum sulfonate	36		B+
Cadmium sulfonate	36		B
Do.	100		B+
Calcium sulfonate (basic)	25		B
Copper sulfonate	18		B+
Do.	36		A
Ferric sulfonate	36		B ²
Do.	75		A
Lead sulfonate	36		B+
Do.	100		A ²
Sodium sulfonate	25		B+

¹ Ratings indicate the area of the surface covered by rust.

A = No rust on strip.

B++ = Trace of rust on strip.

B+ = Less than 5% of surface rusted.

B = 5-25% of surface rusted.

² Test period, 72 hours.

As indicated hereinbefore, the sulfonates of amines having molecular weights in excess of 150 are, for some unexplicable reason, relatively ineffective in the test. Thus, when the sulfonates of dicyclohexylamine and laurylamine, having molecular weights of 181 and 185, respectively, were subjected to the test almost 50% of the surface of the strip was found to be rusted in each case, even with additive concentrations of 100 lbs. of 10% concentrate for each 1,000 bbls. of distillate.

I claim:

1. Method of retarding internal corrosion of pipe lines containing iron which comprises incorporating in the light petroleum distillate charged to the pipe line from 1 to 100 parts per million of a material from the group consisting of petroleum mahogany sulfonic acids and petroleum mahogany sulfonates.

2. Method of retarding internal corrosion of pipe lines containing iron which comprises incorporating in gasoline charged to the pipe line from 1 to 100 parts per million of a material from the group consisting of petroleum mahogany sulfonic acids and petroleum mahogany sulfonates.

3. Method of retarding internal corrosion of pipe lines containing iron which comprises incorporating in kerosene charged to the pipe line from 1 to 100 parts per million of a material from the group consisting of petroleum mahogany sulfonic acids and petroleum mahogany sulfonates.

4. Method of retarding internal corrosion of pipe lines containing iron which comprises incorporating in fuel oil charged to the pipe line from 1 to 100 parts per million of a material from the group consisting of petroleum mahogany sulfonic acids and petroleum mahogany sulfonates.

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