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PREVENTION OF CORROSION

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My invention relates to light petroleum distillate fractions to which anticorrosive properties have been imparted by the addition of exceedingly small proportions of a mixture of a mahogany sulfonate and morpholine.

Rust frequently occurs in light oil products pipe lines, storage tanks and even in the equipment wherein such products are ultimately used, because of the traces of moisture that are inevitably present in the oil. For example, although gasoline as it leaves the refinery is usually free of occluded moisture it may contain as much as 0.005% to 0.01% of dissolved moisture. Part of this dissolved moisture separates when the light oil product is chilled and settles as a separate liquid phase beneath the main body of oil. Water may also enter oil systems along with air through partially filled tanks provided with breather devices. As such a tank cools, for example at night, its contents contract and moisture-laden air is drawn in. This moisture condenses on the walls of the tank, settles to the bottom and dried air is expelled when the contents of the tank again warm up, as from the heat of the sun the next day. Repetition of this cycle eventually leaves appreciable amounts of moisture at the bottom of the tank.

As is obvious, the rust that forms permanently injures expensive equipment and there is additional loss in terms of replacement costs of such equipment and operating time lost during such replacement. For example, where rust forms on interior surfaces of product pipe lines and no effort is made to prevent it, this rust formation may reduce carrying capacity of the pipe by more than 12 per cent in one year. In addition to the decrease in life of rusted equipment such as storage tanks, there is danger of trouble in engine operation from failure of fuel carrying equipment and the likelihood of rust particles clogging carburators or injecting devices for motors and burners, for example.

In the co-pending application of Franklin M. Watkins, Serial No. 86,121, filed April 7, 1949, now Patent No. 2,594,266 issued April 22, 1952, there is disclosed the use of ammonium mahogany sulfonates in light petroleum distillate fractions to impart anticorrosive properties and thereby substantially overcome these problems. Ammonium mahogany sulfonates have been found to be in general a very valuable inhibitor. However I have noted that some distillate fuels are not adequately rust inhibited by even relatively large proportions of ammonium mahogany sulfonates, i. e. proportions as large as 7.0 pounds on the

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oil-free basis per one thousand barrels as shown in Table III.

I have now found that these unusual distillates may be satisfactorily inhibited by addition of a small amount of morpholine with the ammonium mahogany sulfonates. I also have found that in general the use of a small amount of morpholine in combination with ammonium mahogany sulfonates in light distillates results in more effective protection than with either material alone. Thus, when the morpholine inhibitor is added to the light oil in minute amount, only about one fourth, or less, as much of the ammonium mahogany sulfonates are required to effectively inhibit corrosion and the total quantity of inhibitor material added is still only a fraction of the sulfonate that would ordinarily be required alone. For example, about five pounds of ammonium mahogany sulfonates on the oil-free basis are required to effectively inhibit 1000 barrels of a particularly unresponsive kerosine, but by adding about two pounds of morpholine only one pound of the sulfonate is required under the same conditions. In the small amounts employed, i. e. about 2 pounds per 1000 bbls. the morpholine does not affect the quality of the distillate stocks treated. Moreover, with certain stocks, i. e., kerosines, I have found that morpholine acts as a color stabilizer for ammonium mahogany sulfonate inhibited stock. Furthermore, I have found that certain stocks deteriorate when stored under air with the formation of impurities, apparently due to oxidation, which impurities render the stocks less susceptible to corrosion inhibition by ammonium mahogany sulfonate alone but which do not affect the susceptibility of the stocks to corrosion inhibition by a mixture of the sulfonates and morpholine.

The reason for the synergistic activity between the ammonium mahogany sulfonates and morpholine is not understood. Possibly, the sulfonates and morpholine are selectively adsorbed on different portions of the metal surface, although some areas are able to accommodate either, thus more effectively forming an interrupted continuous protective layer. I have observed, however, that with certain fuels it is difficult to obtain complete protection at reasonable concentration with only one of the inhibitors. In such circumstances, I believe that the inhibitor is adsorbed on only certain areas of the metallic surface to the extent of forming an effective protective film, and is incapable of displacing some unusual constituents in the oil which form as films on other areas. These impurities are in-

capable of preventing rust formation on such areas but prevent the inhibitor from forming a protective layer. Accordingly it is my belief that the complete rust protection obtained from use of the combination of inhibitors may be due either to the fact that the secondary inhibitor I employ, i. e. morpholine, is so strongly basic in character that it produces a less corrosive environment or that it displaces the adsorbed polar impurities by chemical action with them to render the impurities harmless or to change them to helpful rust inhibitors.

In my new compositions, it may be that chemical exchange takes place between the ammonium mahogany sulfonate and the more strongly basic morpholine to at least some extent with the liberation of free ammonia and the formation of morpholine mahogany sulfonate. Thus, mixtures of morpholine and ammonium mahogany sulfonates with morpholine are effective for the purposes of my invention.

According to my invention, a small amount of ammonium mahogany sulfonate and morpholine or a mixture thereof is added to the light petroleum distillate fraction. The ammonium mahogany sulfonates may be obtained by reaction of ammonia with sulfuric acid-treated hydrocarbon oils, i. e. by ammoniation of mahogany acids. Such ammonium mahogany sulfonates possess appreciable solubility in both water and hydrocarbon oils. In the practice of my invention, I customarily employ the ammonium sulfonates as a concentrate in the oil from which they are derived. A typical concentrate may have, for example, a sulfonate concentration of about 10 per cent by weight and may test as follows:

Gravity, °API	23.0
Flash, °F	385
Fire, °F	445
Viscosity at 100 SUS	416
Viscosity at 130 SUS	163
Viscosity at 210 SUS	49.2
Viscosity index	90
Color	4½
Nitrogen (per cent)	0.265
Acid number	9.0
Sulfur (per cent)	0.60

This particular concentrate was prepared by treating a mid-continent neutral oil with four successive dumps of oleum, a total of 120 pounds of the oleum being used for each barrel of oil. Following removal of the separable sludge after the last dump of oleum, the acid oil was blown with air to remove sulfur dioxide and settled to remove substantially the last trace of sludge. Thereafter the oil was mixed with 0.5 per cent by weight of water and neutralized with an excess of anhydrous ammonia. Finally the oil was heated to a temperature of 280° F. to dehydrate it, and filtered to obtain the above product.

Although the ammonium mahogany sulfonates are advantageously employed in the oil solution in which they are prepared, the sulfonates may be recovered by extraction with a low molecular weight alcohol, such as isopropanol or ethanol, followed by distillation for use in the oil-free form. The distillation procedure is disclosed in Patent No. 2,461,371, issued February 8, 1949, to Eldon B. Cole. A lower molecular weight oil soluble alcohol, such as isopropanol, or aniline is advantageously added to the sulfonate solution in small amounts to improve the stability thereof. Such ammonium mahogany sulfonate solutions of greater stability are disclosed in the patents issued to M. P. Kleinholz and T. P. Hack, Patents Nos. 2,522,518 (alcohol addition) and 2,522,519 (aniline).

Morpholine, which is added in conjunction with the sulfonates, and which may be obtained commercially at reasonable cost, is a water soluble, hydrocarbon soluble, secondary amine and is itself a rust inhibitor. It is a strong organic base which neutralizes acidic impurities in the light petroleum distillates and the resulting salts also have rust inhibitor properties. In pure form it attacks skin and cork but presents no problem when handled in dilute solution. Although the ammonium mahogany sulfonates and morpholine are not mutually soluble they may be added separately or as a mixture to the light petroleum distillates. By light petroleum distillate I mean petroleum distillates of a viscosity not exceeding that of gas oil. In this way light oils such as gasoline, kerosine or distillate fuels, e. g. home heating fuels or diesel oils, are effectively given anticorrosive properties. The amount of each to be added will vary depending on the type of distillate to be inhibited since the combination will determine the extent of the synergistic action. Where it is necessary to meet color specifications with certain stocks inclining to color instability in storage, it may be desirable to increase the proportion of morpholine employed. Advantageously, the ratio of 0.5 part of ammonium mahogany sulfonates to one part of morpholine is used although I have found in a number of tests that ratios varying from 6.0 to 1 down to 0.5 to 1 give satisfactory results. Ordinarily, amounts of the ammonium mahogany sulfonates in the range of 0.6 to 4.0 pounds per one thousand barrels on the oil-free basis and about 0.4 to 4.0 pounds of morpholine per one thousand barrels are satisfactory. Usually however it is unnecessary to exceed about three pounds of the sulfonates or three pounds of morpholine per 1000 barrels of stock.

Thus, the synergistic admixture of ammonium mahogany sulfonates and morpholine I use affords low cost rust protection when incorporated in light petroleum distillate fractions. It does not require multiple injections into the oil treated—only one injection is needed. This is an important advantage particularly in providing rust protection in light oil products pipe lines which are of great length. Since the combination is chemically stable and does not become inert through oxidation there is no predictable limit to the effectiveness of the anticorrosive product, from the pipe line to the ultimate consumer. That is, the protection against rusting will extend, after a single injection following preparation of the oil, beyond the trunk lines used to transport it from the refinery to bulk distribution plants. The additional equipment subject to protection against rusting includes bulk and service-station equipment, tank cars, tank trucks, and customer equipment. In addition to the increase in useful life due to rust inhibition, there is the additional advantage to the ultimate user of less trouble from rust particles, such as plugging of filters and orifices of carburetors, diesel-engine injectors, and gun-type burners of household heating units. The oil compositions containing it can be handled easily with ordinary equipment and since they give homogeneous, non-toxic products there is no danger to personnel. As noted above, interfering impurities resulting from oxi-

dation may form in some distillate stocks when stored at room temperature under air for any length of time so that when these deteriorated stocks are treated with ammonium mahogany sulfonates, they are less susceptible to corrosion inhibition and tend to discolor. In some instances the inhibiting efficiency of the sulfonates may decline appreciably. I have found that with distillate blends containing both morpholine and ammonium mahogany sulfonate color deterioration is less than that of blends containing only the ammonium mahogany sulfonate. I have also found that base stocks are substantially as susceptible to the combination of inhibitors after four month's storage as they were when fresh. Furthermore, due to the fact that morpholine is more readily extracted into water in contact with inhibited hydrocarbons than are the ammonium mahogany sulfonates, the consequent build-up of morpholine concentrations in water bottoms in storage tanks and pipe lines where the distillate is periodically static gives better rust protection therein than is afforded by ammonium mahogany sulfonates alone.

The following examples are presented in order to illustrate more clearly the improved anticorrosive and other properties of my invention.

The inhibitors were added to distillate fuels, (gasoline, from both Mid-Continent and Pennsylvania crudes, and kerosine and distilled heating oils from Pennsylvania crudes) and tested by a modification of ASTM test D665–47T: "Rust-Preventing Characteristics of Steam-Turbine Oil in the Presence of Water." In this modified procedure, a freshly ground rust test coupon consisting of a ½ inch diameter by 5½ inches long mild steel rod is suspended in a 400-ml. beaker equipped with a stirrer and placed in a temperature controlled bath capable of maintaining the temperature at 100±1° F. The test fuel (350 ml.) is added and stirred for thirty minutes to allow the rust inhibitor to precoat the test specimen. Part (50 ml.) of the test fuel is then removed and 30 cc. of distilled water is added, and the mixture stirred for the 3½ hour test period. At the end of this period, the coupon is removed, dried with suitable solvents, inspected and rated according to the following scale:

A—no rust
B++—trace of rust (covering a maximum of 0.25% of total surface area)
B+—0.25 to 5% of surface area covered by rust
B—5 to 25% of surface area covered by rust
C—25 to 50% of surface area covered by rust
D—50 to 75% of surface area covered by rust
E—75 to 100% of surface area covered by rust

The test conditions are substantially more severe than ordinary conditions encountered so the results give a clear indication of the effectiveness of the inhibitor mixture. Throughout the tests and accompanying description the ammonium mahogany sulfonates were used as the 10 per cent by weight solution described in the specification.

Examples of results available from tests using various light petroleum distillates plus ammonium mahogany sulfonates alone, morpholine alone, and combinations of sulfonates and morpholine are shown in Tables I through IV. The tests demonstrate the combination of ammonium sulfonate and morpholine to be more effective as a rust inhibitor than either inhibitor alone due to the occurrence of a synergistic effect. For example, as is set forth in Table IV, a test run on a No. 3 fuel oil, using 15#/1000 bbls. of ammonium sulfonate rated a C and one using 3#/1000 bbls. of morpholine also rated a C, but these two when used together at these dosages gave a B++ rating. Also when the amount of these inhibitors used alone was more than quadrupled no better than a B+ rating could be obtained. Similar examples in other distillates are shown in the tables.

The inhibitors were added to distillate fuels and also tested in accordance with the following static test procedure. A flat strip of mild carbon steel (⅛" x ½" x 5⅞") is cleaned with naphtha or other solvent to remove grease and oil and then polished with emery cloth until no rust or pits remain. During these polishing operations and subsequently, the strip should be handled with a clean cloth or a piece of Kleenex tissue. After the strip has been thus prepared, it should be carefully wiped free of emery dust. The specimen together with 100 ml. of the sample to be tested are placed in a corked four ounce oil sample bottle which is allowed to lay on its side at room temperature for one hour. The liquid should cover the test specimen during this contact period. Then add 10 ml. of distilled water, cork tightly, and shake vigorously for three minutes to insure water wetting over the entire strip surface. The specimen should be tightly wedged between the cork and the bottom of the bottle to minimize breakage. The bottle is then restored to an upright position and allowed to stand at room temperature. The specimen is examined for rust daily after which the bottle is shaken again to replace water droplets on the specimen in the hydrocarbon phase that may have been disturbed during inspection.

Table V gives results of static tests using a No. 2 fuel oil. These test results show a very great improvement in the amount of protection given in the aqueous phase when morpholine is used in conjunction with an ammonium mahogany sulfonate. An even greater amount of protection is obtained in the hydrocarbon phase.

TABLE I

	10% Ammonium Sulfonate		Morpholine	
	Concentration, Lbs./1000 Bls.	Rating	Concentration, Lbs./1000 Bls.	Rating
Effect of each of the inhibitors alone in a gasoline fraction: (from a mid-continent crude.)	6	B	----------	----------
	22	B+	----------	----------
	25	A	----------	----------
	----------	----------	1.2	E
	----------	----------	6	B+
	----------	----------	12	A
Combined effect of both inhibitors in the same gasoline fraction:	4	----------	0.8	B
	6	----------	1.2	B++
	18	----------	0.4	B++
	12	----------	0.6	B+
	9	----------	0.9	B+

TABLE II

	10% Ammonium Mahogany Sulfonates		Morpholine	
	Concentration, Lbs./1000 Bls.	Rating	Concentration, Lbs./1000 Bls.	Rating
Effect of each of the inhibitors alone in a gasoline fraction: (from a Pennsylvania crude.)	15	C		
	25	B+		
	35	A		
			3	D
			6	B
			18	B+
Combined effect of both inhibitors in the same gasoline fraction:	20		2.5	B+
	15		3	B++

TABLE III

	10% Ammonium Sulfonate		Morpholine	
	Concentration, Lbs./1000 Bls.	Rating	Concentration, Lbs./1000 Bls.	Rating
Effect of each of the inhibitors alone in a kerosine fraction:	10	B		
	35	B+		
	70	B+		
			2	E
			12	B
			18	B+
Combined effect of both inhibitors in the same kerosine fraction:	20		1	B+
	30		0.5	B+
	10		2	B++
	25		1.5	B++
	50		1	A

TABLE IV

	10% Ammonium Sulfonate		Morpholine	
	Concentration, Lbs./1000 Bls.	Rating	Concentration, Lbs./1000 Bls.	Rating
Effect of each of the inhibitors alone in a No. 3 Fuel Oil fraction:	15	C		
	40	B+		
	70	B+		
			3	C
			12	B+
Combined effect of both inhibitors in the same fuel oil fraction:	10		2	B+
	15		3	B++
	30		2.5	B++

TABLE V

Rust inhibitor evaluation by static tests using a No. 2 fuel oil

	10% Ammonium Sulfonate Concentration Lbs./1000 Bls.	Morpholine Concentration Lbs./1000 Bls.	Average Failure Time in Hours [1]	
			Hydrocarbon Phase	Water Phase
Effect of each of the inhibitors alone in a No. 2 Fuel Oil fraction:	None	None	30	1.5
	12		164	95
	28		760	175
		2.4	216	210
		18	2,700	1,932
Combined effect of both inhibitors in a No. 2 Fuel Oil fraction.	12	2.4	7,728+	3,601
Combined effect of both inhibitors in a gasoline fraction.	18	18	15,864+	15,864+

[1] Average of 4 tests on each blend. Failure time is reported as the number of hours required for rust to form on more than 5% of the area covered by hydrocarbon or more than 25% of the area covered by water.

I claim:

1. Light petroleum distillate fractions into which have been incorporated amounts in the range approximating 0.6 to 4.0 pounds of ammonium mahogany sulfonates on the oil-free basis and 0.4 to 4.0 pounds of morpholine, each per one thousand barrels of petroleum distillate.

2. Light petroleum distillate fractions into which have been incorporated amounts in the range approximating 0.5 to 2.0 pounds of ammonium mahogany sulfonates on the oil-free basis and 0.4 to 4.0 pounds of morpholine, each per one thousand barrels of petroleum distillate.

DAVID B. SHELDAHL.

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