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PREVENTION OF RUST IN PIPE LINES AND TANKERS WITH ESTER-TYPE WAX OXIDATE

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9 Claims. (Cl. 44—70)

This invention relates to preventing or retarding the rusting of iron bodies in contact with corrosive petroleum hydrocarbon liquids, such as gasoline, kerosene, diesel fuel and furnace oil. It is particularly concerned with preventing or retarding the rusting of iron pipe lines, and iron tanks as in tanker ships used to transport light petroleum distillates of the above type. However, the principles may also be applied in other fields, as in protecting from corrosion heat exchangers carrying petroleum hydrocarbons.

Rusting frequently occurs in pipe lines and storage tanks when containing gasoline or other light distillates. This is in part believed due to moisture which is present in the pipe line or tank along with the distillate. Many chemical additives have been incorporated in light distillates to prevent or retard rusting. However, in the past it has not been possible to obtain completely satisfactory protection at a reasonably low cost.

Among the additives which have been suggested is oxidized microcrystalline wax (petrolatum). While this material may give fair results in preventing rust, it has several undesirable drawbacks which are surmounted by the present invention. Among these drawbacks are:

(*a*) It has an excessively high viscosity, and thus is hard to dissolve and must be cut back with a great deal of solvent.

(*b*) It has a dark color which undesirably darkens gasoline and other light distillates.

(*c*) It increases gum values on gasolines undesirably.

(*d*) It imparts a cloudy appearance to gasoline.

(*e*) It emulsifies with water and may cause water in a pipe line or tanker to become dispersed in the gasoline or other light distillate.

We have discovered that improved corrosion inhibition at low cost is obtained without the drawbacks listed above by incorporating in a light petroleum distillate high ester content light colored oxidized macrocrystalline wax having a neutralization number (Neut. No.) above 60, a saponification number (Sap. No.) above 200, a Neut. No. to Sap. No. ratio between 0.25 and 0.4 and an unsaponifiable content less than about 40%.

The amount of the ester type oxidized macrocrystalline wax included in the distillate may range from .5 to about 50 pounds per thousand barrels of distillate without adversely affecting distillate color. Typical concentrations that have been found highly useful in preventing rusting of iron surfaces are 3 to 5 lbs. of oxidate per thousand bbls. of light distillate passed through a pipe line; and about 12 to 18 lbs. of oxidate per thousand bbls. of light distillate in a tanker. The higher concentration is required in a tanker because the distillate is non flowing, so that water tends to separate out and accumulate in the bottom of the tanks where it causes excessive corrosion. In a pipe line, on the other hand, water particles tend to remain suspended in the flowing distillate and cause less corrosion, thus requiring less oxidate. Also, in a tanker highly corrosive sea water may be present, whereas a pipe line usually contains less corrosive fresh water.

For introducing the oxidate into a light distillate, it is advantageous to form first a concentrated additive solution of the oxidate in a solvent which is also soluble in the distillate to be inhibited. Such a solvent may be a light petroleum fraction such as benzene, toluene, kerosene, or light diesel and gas oil fractions. A preferred solvent is an untreated kerosene distillate having a gravity of about 30° API, a flash point of about 160° F. (TCC), and an ASTM distillation 50% point of about 475° F. Proportions of about one part by weight of oxidate to two parts by weight of petroleum fraction are satisfactory, although other proportions may be used successfully. This step is advantageous because the oxidate is normally solid at room temperature and cannot be introduced directly into the light distillate in uniform proportions.

PREPARATION OF ESTER-TYPE MACROCRYSTALLINE WAX OXIDATE

Details of preparation of a suitable oxidized macrocrystalline wax are disclosed in co-pending application Serial No. 427,653, filed May 4, 1954, by John K. McKinley, Roy F. Nelson, and Gordon S. Bright, now abondoned. As described therein, high ester content macrocrystalline wax oxidates of low unsaponifiable content and excellent oil solubility are obtained by reacting a deoiled paraffin wax containing less than 5 per cent oil with air in the presence of a catalyst at an air velocity of 1.5 to 6 feet per second, equivalent to an air rate of 8 to 35 cubic feet per pound of wax per hour, at a temperature between 300 and 350° F., and at a pressure below 25 pounds per square inch absolute. The wax oxidates obtained by the use of the prescribed processing conditions in a period of 4 to 10 hours are characterized by a Neut. No. above 60 and usually between 70 and 100, a Sap. No. above 200 and usually between 210 and 300, a Neut. No. to Sap. No. ratio between 0.25 and 0.4, unsaponifiable content less than 40 percent, and good solubility in hydrocarbon fractions.

The deoiled paraffin wax prescribed as a charge material is derived from lubricating oil distillates, is macrocrystalline in character, is predominantly aliphatic in nature, and contains between 20 and 33 carbon atoms per molecule. The preferred paraffin wax for use in this invention contains an average of 25 to 30 carbon atoms per molecule. Deoiled paraffin waxes meeting the specification of less than 5 percent oil are available as by-products of the manufacture of low pour lubricating oils. The deoiled wax is obtained from distillate lubricating oil fractions by solvent dewaxing or by pressing and sweating, and usually contains less than 3 percent oil. A preferred charge material for the process of the invention is obtained by solvent dewaxing a distillate oil which has been solvent refined with a solvent such as furfural, phenol, etc. A semi-refined wax of 125 to 127° F. melting point obtained by solvent dewaxing a lube oil distillate is an example of a preferred charge material.

The importance of the charge material in determining the characteristics of the resulting oxidate is demonstrated by comparison of properties of the oxidates obtained under similar reaction conditions by oxidation of a semi-refined 125 to 127° F. melting point macrocrystalline paraffin wax isolated from a waxy paraffin distillate by solvent dewaxing, and of a petrolatum or microcrystalline wax having a 151.8° F. melting point and isolated from a refined residuum by centrifuge dewaxing. In Table I, there are shown the properties of the oxidates obtained from the afore-described petrolatum and paraffin wax in 6 and 4 hours, respectively, by air oxidation at a tem-

perature of 330° F., at atmospheric pressure, at an air velocity of 3 feet per second, equivalent to an air rate of 20 cubic feet per pound per hour, and with 0.4 weight percent $KMnO_4$ as a catalyst.

Table I

	Petrolatum Oxidate	Paraffin Wax Oxidate
Neut. No.	29	85
Sap. No.	122	235
Neut. No./Sap. No. ratio	0.24	0.36
Unsaponifiable Content, percent	32	33
SUS Viscosity at 210° F.	7,000	100

In general, the production of ester-type, oil-soluble wax oxidates is effected in an aluminum-lined reactor in the presence of a catalyst. A particularly preferred catalyst is potassium permanganate which is charged to the reactor in 3 to 10 percent aqueous solution together with deoiled paraffin wax, in amounts ranging from 0.1 to 1.0 percent of the total hydrocarbon charge. Oil-soluble catalysts such as manganese stearate, zinc stearate, and manganese and zinc salts of previously oxidized wax fractions may also be employed in the process of this invention to produce the desired ester-type, oil-soluble macrocrystalline wax oxidates of low unsaponifiable content.

The oxidation temperature must be maintained between 300 to 350° F. in order to produce an oxidate of desired characteristics. When the temperature is in the prescribed range and the other reaction conditions are observed, the Neut. Nos. of the product either slightly decrease or substantially level out as reaction times increase from 4 to 13 hours, while the Sap. Nos. steadily increase until they reach a maximum somewhere in the neighborhood of 10 to 13 hours. The effect of higher temperatures on the properties of oxidates from deoiled paraffin wax, while maintaining the other prescribed conditions, is particularly surprising. Temperatures in the range of 350 to 400° F. produce a paraffin wax oxidate whose Neut. Nos. are much lower and whose Sap. Nos. are substantially lower than the product obtained at the 300 to 350° F. range. In addition, the oxidate obtained at the higher temperature range has a higher unsaponifiable content and a much lower Neut. No. to Sap. No. ratio. When oxidation is effected at the 350 to 400° F. range, the Neut. Nos. progressively decrease with reaction time, while the Sap. Nos. remain constant. Temperatures below 300° F. give an oxidate of higher unsaponifiable content, poorer solubility and greater acidity.

Pressures below 25 p. s. i. a., and preferably atmospheric pressure, are prescribed in order to produce the high ester content oil-soluble oxidate of the invention. Pressures above the prescribed 25 p. s. i. a. limit result in the production of more acidic oxidates with Neut. No. to Sap. No. ratios above 0.45.

The final decisive factor in the production of the desired oxidates is the rate at which air is passed through the deoiled macrocrystalline paraffin wax. Air velocities of approximately 1.5 to 6 feet per second should be employed in order to obtain the desired ester-type, oil-soluble oxidate of low unsaponifiable content.

In pilot unit operation, the prescribed 1.5 to 6 feet per second air velocity through a 150 pound charge is obtained using an air rate of 20 to 35 cubic feet per pound, per hour, while in a larger plant unit holding 3000 pounds of charge the required air velocity is obtained using air rates of 8 to 20 cubic feet per pound per hour. Thus, for both pilot and plant operation, the air rates fall in the range of 8 to 35 cubic feet per pound of wax per hour, the plant air rate usually being half of that used in the pilot plant. The air velocity required for the production of the desired ester-type oxidate is the same in both pilot and plant operation.

At air velocities above the prescribed ranges, even though other reaction conditions are observed, the resulting wax oxidates have reduced oil solubility and a higher acid content with resulting higher Neut. No. to Sap. No. ratios. At air velocities below the prescribed ranges, the unsaponifiable content is very high, generally above 50 percent, and both the Neut. Nos. and Sap. Nos. are low and increase with reaction time. The Neut. Nos. increase from about 14 to about 36 at reaction times between 4 and 13 hours, while the Sap. Nos. increase from about 50 to 135 as the oxidation time varies over the same period. Apparently, the use of air velocities and air rates in the prescribed ranges in conjunction with the use of prescribed temperature and pressure conditions effects the proper correlation of agitation and contact of the reactants to produce a high ester-type, oil-soluble oxidate from a deoiled paraffin wax. It is important to note that in both pilot and plant operation the amount of air passed through the reaction mixture is considerably in excess of that which reacts with the deoiled paraffin wax.

The desired oxidate is produced in a period of about 4 to 10 hours by the process of this invention. When the reaction temperature, pressure and air velocity are in the upper portion of the prescribed ranges, the desired product is obtained in a period within the lower portion of the prescribed 4 to 10 hour range; whereas when lower temperatures, pressures and air rates within the prescribed ranges are employed, a longer reaction period is required. When the oxidation is effected at an air velocity of about 3 feet per second, a temperature of about 330° F. and atmospheric pressure, an oxidate having a Sap. No. of about 220 to 270, a Neut. No. in the range of 70 to 90 and an unsaponifiable content of about 25 to 40 percent is obtained in about 4 to 6 hours.

The process for producing the ester type macrocrystalline wax oxidate used in the present invention is illustrated in the following example showing oxidation of deoiled paraffin wax at the prescribed reaction conditions.

EXAMPLE I

There was charged to a 12-foot high pilot plant reactor having an internal diameter of 10 inches 150 pounds of a deoiled macrocrystalline paraffin wax obtained by solvent dewaxing a lubricating oil distillate of SAE 20 grade. The charge wax had the following properties:

Gravity, ° API	43.6.
Flash, COC, ° F.	410.
Visc. SUS at 210° F.	38.
English melting point, ° F.	126.
Ash	None.
Oil, percent (ASTM)	About 0.7.
Petrolatum melting point, ° F.	124.5.
Fire, COC, ° F.	470.

There was also charged to the reactor enough of an aqueous solution of potassium permanganate to provide a concentration of 0.4 percent. The reaction mixture was rapidly heated to a temperature of about 350° F. and then was maintained at a temperature of about 330° F. and at atmospheric pressure. Air was passed through the mixture at an air velocity of about 4.5 feet per second, equivalent to an air rate of about 30 cubic feet of air per pound of paraffin wax per hour in the pilot unit. The reaction was continued for a period of about 7 hours to give an oxidate having the following characteristics:

Neut. No.	82
Sap. No.	270
Ratio, Neut. No./Sap. No.	0.30
Unsap, percent	34.6
Gravity, ° API	13.6
Visc. SUS at 210° F.	268

The same charge material was oxidized under the same reaction conditions with the exception that the oxidation was continued for 10 to 13 hours. The oxidates obtained after 10 and 13 hours had the following properties:

	Hours of Oxidation	
	10	13
Neut. No.	74	72.2
Sap. No.	262	263
Ratio, Neut. No./Sap. No.	0.28	0.27
Unsap. percent	27.6	21.3
Gravity, °API	12.8	11.5
Visc. SUS at 210° F.	686	887

The process is also applicable to other deoiled macrocrystalline paraffin waxes containing less than 5 percent oil such as crude scale waxes, and slack wax. The important factor in selection of the charge wax is that it be macrocrystalline in character, derived from a paraffin base distillate oil, and have an oil content less than 5 percent and preferably less than 3 percent.

In the foregoing description the term "air velocity" means superficial velocity, that is, the velocity of the air flowing through the reaction vessel at reaction temperature and pressure in the absence of wax, catalyst or other interior obstruction.

CORROSION INHIBITION

The principles of the invention as applied to corrosion inhibition will be illustrated by the following specific examples which demonstrate the improved results obtained when inhibiting gasoline by incorporating therein high ester content oxidized macrocrystalline wax produced in accordance with the process described in detail above. The particular oxidate used to exemplify the invention was produced with an oxidation time of five and one half hours, a temperature of 330° F., atmospheric pressure, and an air rate of 30 standard cubic feet per hour per pound when using 0.4% of potassium permanganate as the catalyst. It was light in color, had a Neut. No. of 79, a Sap. No. of 233, contained 33% unsaponifiables, had a viscosity of 247, SUS at 210° F., and had an API gravity of 15.8.

This oxidate was incorporated in kerosene in proportions of one part by weight of oxidate to two parts by weight of solvent, for subsequent addition to the light distillate requiring inhibition. However, proportions given below are of the undiluted oxidate.

EXAMPLE II.—RUSTING TEST

In this test a mixture of 300 ml. of gasoline with 30 ml. of distilled or synthetic sea water was shaken at a temperature of 80° F. for three hours with a cylindrical steel specimen completely immersed therein. Conditions otherwise were as described in ASTM test D–665–49T.

When using distilled water it was found that 1 lb. of oxidate per thousand bbls. of gasoline completely protected the steel specimen from rusting. The test specimen had no rust, as contrasted to 25% rust on a blank test specimen run without any oxidate.

When using synthetic sea water it was found that in gasoline containing 3 lbs. of oxidate per thousand barrels the steel specimen only carried 5% of rust, in contrast to 75% of rust on a blank specimen run without any additive.

The following table shows the improved results obtained with the oxidates of the present invention compared with petrolatum oxidate in the above-described rusting test.

Table II

PERCENT RUST WITH SYNTHETIC SEA WATER

Dosage, lb./thousand bbls.	0	1	3	6
PERCENT RUST ON TEST SPECIMENS				
Ester Type Wax Oxidate	40	1	0	0
Ester type Petrolatum Oxidate (Neut. No. 28; Sap. No. 125)	40	10	4	5
Acid type Petrolatum Oxidate (Neut. No. 112; Sap. No. 216)	40	10	10	0

EXAMPLE III.—QUICKIE CORROSION TEST

In this test a polished steel strip is placed in a four ounce bottle containing 115 cc. of the test distillate at 90° F. The strip and distillate are then allowed to stand for 15 minutes. Next, 20 cc. of oil are poured out and 20 cc. of distilled or synthetic sea water are added to the bottle, and the bottle is shaken for 15 seconds in a horizontal position. The bottle is then turned to vertical position, given a short swirl to wash the water from the strip and placed upright. Readings of the percentage of rust on the strip in the distillate phase are taken after three hours.

When conducting the test using distilled water, it was found that a blank specimen showed 40% rust, whereas when using 5, 10 and 15 lbs. of oxidate per thousand bbls. the percentage of rust on the strips was reduced to 3, 1 and 1% respectively.

When using synthetic sea water the blank specimen showed 40% of rust, whereas 10 and 15 lbs. of oxidate per thousand bbls. reduced the percentage of rust to 9 and 3% respectively.

EXAMPLE IV.—14 DAY CYCLING TEST

This test procedure simulates tanker transportation service between a Texas refinery and an east coast port when gasoline is hauled north and the return voyage is made under water ballast. The method consists of immersing for seven days in a tall 4 oz. bottle a weighed polished steel strip in contact with 5 cc. of synthetic sea water and 110 cc. gasoline. The liquids are then removed and 115 cc. fresh salt water is added, after which there is an additional seven day storage period. The steel strip is then removed, cleaned and reweighed. The bottles are kept in an oven at 90° F. for the storage period.

A blank run without any inhibitor showed 68.8 milligrams of weight lost after 14 days, whereas when using 12 lbs. of oxidate per thousand bbls. the test specimen only showed 31.7 milligrams of weight lost. This amounted to a 54% reduction in weight loss over the blank.

With the ester type macrocrystalline wax oxidate of the present invention best results are obtained when the Neut. No. falls within the range 75–100. When the Neut. No. is greater than 100, materials are present which are insoluble in kerosene and other light petroleum fractions.

The effects of increasing Neut. No. were shown in quickie corrosion tests on three samples, as follows:

EXAMPLE V

	Sample		
	A	B	C
Oxidation Conditions:			
Time, Hrs.	2	4	6
Temp., °F.	330	330	330
Tests on Product:			
Neut. No.	46	76	88
Sap. No.	132	214	242
NN/SN Ratio	0.348	0.354	0.362
Percent Non Sap.	56.4	40.2	30.1
Visc. SUS at 210° F.	50.2	77.4	124.8
Dosage Inhibitor, Lbs./M bbls.	10	10	10
Quickie Corrosion Test—Results Using Gasoline and Synthetic Sea Water:			
Visual Percent Rust On Iron Strips—			
After 3 Hours	15	7	3
After 1 week	43	13	6

In the above examples gasoline was used as the test liquid because it is well known to be the most corrosive liquid transported in pipe lines and tankers. Obviously when gasoline is effectively inhibited by a selected oxidate, it can be expected that other less corrosive distillates will also be inhibited by the same oxidate.

EXAMPLE VI.—EMULSIFICATION

Equal portions of ester type petrolatum and macrocrystalline wax oxidates were placed in water in glass containers and shaken vigorously. A completely stable emulsion was formed with the former, whereas with the latter some emulsification was obtained which separated in only a few minutes.

In color the ester type macrocrystalline wax oxidate is far lighter than ester type oxidates of petrolatum, which are reported as dark brown or black. On the Lovibond ½ inch scale the color of a petrolatum oxidate has been reported as high as 6,000.

Additionally, the ester type macrocrystalline wax oxidate gives less trouble from gum formation in gasoline than does the petrolatum oxidate. In a standard ASTM gum test conducted in the laboratory, after 6 months of storage the gum from gasoline containing 15 pounds per thousand barrels of ester type petrolatum oxidate was 11 mgs./100 cc., whereas ester type macrocrystalline wax oxidate under the same conditions gave only 4 mgs./100 cc.

From the foregoing laboratory test results it is apparent that the present invention provides an important improvement in preventing the corrosion of iron in the presence of light petroleum distillates. The ester type macrocrystalline wax oxidate of this invention also has been used experimentally in sea going tankers and in pipe lines. Visual observation has indicated that the predicted protection based on the laboratory tests has been realized, and rusting has been greatly reduced. In one pipeline transporting gasoline, test coupons indicate that essentially no corrosion has occurred during an experimental period of several months when using 3 pounds of oxidate per thousand barrels of gasoline. In an oil tanker rusting was greatly reduced when using experimentally 12 and 18 pounds per thousand barrels, respectively, during two periods of operation when cargoes included gasoline, kerosene, fuel oil, lubricating oil, and diesel fuel.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A composition consisting essentially of a light petroleum distillate having incorporated therein in a rust inhibiting amount, oxidized macrocrystalline paraffin wax having a Neut. No. between 60 and 100, a Sap No. between 200 and 300, a Neut. No. to Sap. No. ratio between 0.25 and 0.4, and an unsaponifiable content less than about 40%.

2. A composition in accordance with claim 1 wherein said oxidized wax is present in an amount between about .5 and about 50 pounds per thousand barrels of distillate.

3. A composition in accordance with claim 1 wherein said macrocrystalline wax contains 20 to 33 carbon atoms.

4. A rust inhibiting additive for incorporation with a light petroleum distillate for preventing rusting of iron pipe lines, tanks, and the like containing said distillate, said additive consisting essentially of about 1 part by weight of oxidized macrocrystalline paraffin wax having a Neut. No. between 60 and 100, a Sap. No. between 200 and 300, a Neut. No. to Sap No. ratio between 0.25 and 0.4, and an unsaponifiable content less than about 40%, dissolved in about 2 parts by weight of a light petroleum solvent.

5. A composition consisting essentially of a light petroleum distillate having incorporated therein in a rust inhibiting amount, oxidized macrocrystalline paraffin wax having a Neut. No. between about 70 and 90, a Sap. No. between about 220 and 270, a Neut. No. to Sap. No. ratio between 0.25 and 0.4, and an unsaponifiable content between about 25 and 40%.

6. A composition in accordance with claims 5 wherein said oxidized wax is present in an amount between about .5 and about 50 pounds per thousand barrels of distillate.

7. A composition in accordance with claim 5 wherein said macrocrystalline wax contains 20 and 33 carbon atoms.

8. A rust inhibiting additive for incorporating with a light petroleum distillate for preventing rusting of iron pipe lines, tanks, and the like containing said distillate, said additive consisting essentially of about 1 part by weight of oxidized macrocrystalline paraffin wax having a Neut. No. between about 70 and 90, a Sap. No. between about 220 and 270, a Neut. No. to Sap. No ratio between 0.25 and 0.4, and an unsaponifiable content between about 25 and 40%, dissolved in about 2 parts by weight of a light petroleum solvent.

9. A composition consisting essentially of a corrosive petroleum hydrocarbon liquid having incorporated therein a rust inhibiting amount, oxidized macrocrystalline paraffin wax having a Neut. No. between 60 and 100, a Sap. No. between 200 and 300, a Neut. No. to Sap. No. ratio between 0.25 and 0.4, and an unsaponifiable content less than about 40%.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,862,802 December 2, 1958

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 24, for "claims" read -- claim --; line 28, for "20 and 33" read -- 20 to 33 --.

Signed and sealed this 17th day of March 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

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Commissioner of Patents