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HYDROCARBON COMPOSITIONS CONTAINING THE WATER-INSOLUBLE NITRIC ACID OXIDATION PRODUCT OF HYDROCARBONS

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This invention relates to anti-rust agents for hydrocarbon compositions and hydrocarbon compositions containing the same, and more particularly, it relates to hydrocarbon compositions containing the water-insoluble nitrogen-containing product resulting from the oxidation of saturated aliphatic hydrocarbons with nitric acid.

Rusting of ferrous metals due to the presence of water as a contaminant in some hydrocarbon compositions is a serious problem in the storage, handling and use of such compositions. Although gasoline, oil and other hydrocarbons derived from petroleum are substantially free from moisture when they leave the refinery, traces of water may later be found in these products. Liquid petroleum products are frequently removed from storage tanks by water displacement, thus giving rise to the possibility of water contamination. In other instances, water can be introduced into pretroleum products through faulty tank closures. Storage tanks for petroleum hydrocarbons because of their volatility must be constructed to allow room for expansion and must be provided with adequate breathing devices. Thus, as the contents of the tank contract, at night, for example, moist air is drawn in. The moisture thus drawn in condenses and settles to the bottom of the tank. The next day as the tank heats up the contents of the tank expand thus forcing out dried air. As this cycle is repeated day after day, appreciable amounts of water are collected in the bottom of the tank. Water contamination is particularly a problem in humid atmospheres such as those encountered in the tropics and on the seaboard as well as on board ships.

In accordance with the present invention, a hydrocarbon composition is provided which gives prolonged protection against rusting normally resulting when metals are exposed to hydrocarbon compositions containing water as a contaminant.

We have discovered that a hydrocarbon composition can be improved with respect to its anti-rust characteristics by incorporating in said hydrocarbon composition a small amount of the water-insoluble nitrogen-containing reaction product obtained by contacting a saturated aliphatic hydrocarbon under oxidizing conditions with nitric acid. Our invention, based on this discovery, thus comprses a hydrocarbon composition containing an anti-rust improving amount of the water-insoluble nitrogen-containing reaction product obtained by contacting a saturated aliphatic hydrocarbon under oxidizing conditions with nitric acid.

The hydrocarbon compositions to which the anti-rust agent can be added in accordance with the invention can vary in volatility from light gasoline to heavy oils and greases. Within this volatility range we intend to include diesel fuels, lubricating oils, slushing oils, turbine oils, transformer oils, and the like. The gasoline can be a synthetic gasoline, a straight-run gasoline, a cracked gasoline, or blends thereof, and it can contain components obtained from processes other than cracking, such as components obtained from alkylation, isomerization, hydrogenation, polymerization, hydrodesulfurization, hydroforming, "platforming," or combinations of two or more such processes.

When the hydrocarbon composition to which the anti-rust agent is added is gasoline the gasoline can contain minor amounts of addition agents other than the anti-rust agent of the invention. Thus, for example, the gasoline can contain octane improving amounts of tetraethyl lead fluid. Other addition agents normally added to gasolines for a specific purpose such as an anti-oxidant, a haze inhibitor, an oiliness agent, an anti-stalling agent, a corrosion inhibitor, a lead scavenging agent, a dye, etc., can be employed without adversely affecting the improved anti-rust characteristics derived in accordance with the invention.

When the hydrocarbon composition to which the anti-rust agent is added is a lubricating oil the oil can be any oil having a viscosity within the range of common lubricating oils. The oil can be a synthetic oil or a mineral oil including refined or semi-refined paraffinic, naphthenic or asphalt base oil having a viscosity of about 50 to about 4000 SUS at 100° F. If desired, the anti-rust agent can be added to a blend of oils of suitable viscosity instead of a single oil by means of which any desired viscosity within the range of 50 to 4000 SUS at 100° F. can be secured.

When a lubricating composition is desired the lubricating oil can contain minor amounts of an addition agent other than the anti-rust agent of the invention. Thus, for example, it is particularly advantageous in many instances to add an anti-foam agent to the lubricating composition. Other addition agents normally added to lubricating oils for a specific purpose such as an anti-oxidant, pour point depressant, corrosion inhibitor, viscosity index improver, oiliness and extreme pressure agent, and the like, can be employed without adversely affecting the improved anti-rust characteristics derived by the composition of this invention.

The optimum amount of the water-insoluble nitrogen-containing product employed in any given material will vary somewhat depending upon the particular hydrocarbon composition employed and upon the severity of the rust-inducing conditions encountered. The amount of the water-insoluble nitrogen-containing reaction product employed in a liquid hydrocarbon composition can comprise about 1 to about 20 pounds per thousand barrels of hydrocarbon. When the hydrocarbon composition is gasoline, we have obtained highly satisfactory anti-rust characteristics when the water-insoluble nitrogen-containing reaction product was employed in amounts of from 2 to 15 pounds per thousand barrel. When the hydrocarbon composition is a slushing oil, the water-insoluble nitrogen-containing compound can be employed in amounts of about 0.5 to about 10 percent, or more, the upper limit being governed by economics with respect to the cost of the composition. Highly satisfactory results have been obtained with a Texas oil containing about 1 to about 5 percent by weight of the water-insoluble nitrogen-containing compound. In any event, we employ an amount of the water-insoluble nitrogen-containing reaction product sufficient to inhibit or substantially prevent the rusting of ferrous metal surfaces normally encountered when the hydrocarbon composition contains no such reaction product. We have found that the incorporation of this reaction product in gasoline in amounts of about 15 pounds per thousand barrels has no deleterious effect on the other desirable characteristics of the fuel.

When a saturated aliphatic hydrocarbon is oxidized in the presence of a strong oxidant such as nitric acid, the resulting reaction mass comprises a water-soluble portion and a water-insoluble portion. The water-soluble

portion comprises dibasic carboxylic acids. The production of dibasic acids by the nitric acid oxidation of hydrocarbons is known in the art and does not constitute a part of this invention. When nitric acid is used as the oxidant, the water-insoluble portion comprises certain nitrogen-containing hydrocarbons, the exact structural formula of which has not been completely determined. The nitrogen content of the water-insoluble reaction product thus obtained comprises about 0.5 to about 7.0 percent by weight of the reaction product. The nitrogen substituted compounds thus obtained when present in petroleum hydrocarbons, even in exceedingly small amounts, have the property of inhibiting the rusting of iron and steel surfaces.

The process of oxidizing a saturated aliphatic hydrocarbon can be effected in a single stage or in two stages either at atmospheric or elevated pressures. The two stage oxidation is particularly advantageous in that the amount of nitric acid employed can be maintained at a minimum. A particularly desirable process wherein the amount of nitric acid is maintained at a minimum is defined in a co-pending application Serial No. 376,616, now U. S. Patent No. 2,771,482, filed on August 26, 1953, by G. P. Brown, Jr., E. I. Crowley and N. W. Franke. According to the two stage process, a saturated aliphatic hydrocarbon is subjected to oxidation with air or other oxygen-containing gas for a time sufficient to obtain a product having a saponification number above about 100. The oxidized product thus obtained is then subjected to further oxidation at an elevated temperature with nitric acid having a concentration above about 50 percent for a time sufficient to obtain substantial yields of dibasic acids while admixing with the gaseous mixture comprising nitrogen oxides formed during said nitric acd reaction an oxygen-containing gas in amounts and for a time sufficient to regenerate said nitrogen oxides.

Oxidation of saturated aliphatic hydrocarbons can be readily effected at a temperature of 100° to about 400° C. The reaction can be carried out at a constant temperature or the temperature can be varied with time. For example, the reaction can be started out at a low temperature of about 50° C., and the temperature gradually raised to a selected maximum temperature and the reaction can be discontinued when the maximum temperature is reached or the reaction can be maintained at the selected maximum temperature for the desired length of time. While the process can be carried out at atmospheric pressure, elevated pressures to about 1000 pounds per square inch gauge can be used. The amount of air necessary to obtain the air-oxidized product is not critical and can vary from about 2.5 grams to about 10 grams per gram of air-oxidized product obtained. If oxygen is used, about 0.5 gram to about 2.0 grams per gram of air-oxidized product is sufficient.

The concentration of the nitric acid employed in the oxidation of the saturated aliphatic hydrocarbon is not critical, although it should be high enough to convert a substantial amount of the saturated aliphatic hydrocarbon to a dibasic carboxylic acid in a reasonable length of time. Thus, the concentration of the nitric acid is advantageously above about 50 percent and preferably above about 60 percent.

The ratio of nitric acid to the saturated aliphatic hydrocarbon is not critical, provided sufficient acid is present for the desired oxidation. In general, a ratio of about 2.5 to about 20 parts of aqueous nitric acid per part of air-oxidized hydrocarbon is satisfactory when the two-stage oxidation is utilized.

The time required for the substantial completion of the reaction will depend, of course, upon the selection of variables defined hereinabove. Since the reaction is exothermic, from a practical point of view the time required will depend, to a large part, upon the rate at which heat produced can be removed from the reaction system. A period of at least about ½ hour and preferably about 1 to about 100 hours is generally satisfactory to convert a saturated aliphatic hydrocarbon to the corresponding dibasic carboxylic acid. Simultaneously with this reaction water-insoluble nitrogen-containing hydrocarbons are formed. It is the latter products with which this invention is concerned.

The saturated aliphatic hydrocarbons which we can use as starting materials to obtain the desired water-insoluble nitrogen-containing product for use in accordance with the invention are those hydrocarbons boiling above about 250° F. and having eight or more carbon atoms. Saturated aliphatic hydrocarbons having from about 10 to about 40 carbon atoms are particularly desirable because of the relative ease with which they can be oxidized. Included among the saturated aliphatic hydrocarbons which can be employed are petroleum waxes, petrolatum, paraffinic oils, foots oil, oils and waxes obtained from the Fischer-Tropsch process, n-octane, decane, cetane, etc. We can also employ charge stocks which are predominantly saturated aliphatic hydrocarbons and which can contain cycloparaffins. The petroleum waxes are particularly good starting materials.

The oxidizing action necessary to produce appreciable yields of water-soluble dibasic acids and water-insoluble nitrogen-containing compounds must be strong and therefore mere air blowing will not suffice, although an oxygen-containing gas such as air in combination with nitric acid can be employed to reduce the consumption of nitric acid. In such a case an amount of air to give 100 percent by weight of molecular oxygen based upon the nitric acid can be employed. While any strong oxidant can be used where the sole desired product is a dibasic carboxylic acid, only nitric acid can be used to give the desired water-insoluble nitrogen-containing compound employed in accordance with this invention. The oxidation of saturated aliphatic hydrocarbons to produce the water-insoluble nitrogen-containing product employed in accordance with the invention can be conducted with or without the aid of an oxidation-promoting catalyst. Included among the oxidation-promoting catalysts which can be used are ammonium metavanadate and cobalt nitrate.

The following examples will illustrate the preparation of compounds useful in our invention. Example 1 will illustrate the nitric acid oxidation of paraffin wax in a single stage. Examples 2 and 3 will illustrate the nitric acid oxidation of paraffin wax in a two-stage process.

EXAMPLE 1

200 grams of a 132° F. melting point refined paraffin wax and 1000 grams of 90 percent nitric acid were charged to a stainless steel rocking autoclave which was then sealed. The autoclave and contents were heated to 110° C. in a period of about ½ hour. This temperature was maintained for an additional hour during which time the maximum pressure attained was 424 pounds per square inch gauge. The autoclave and contents were then cooled to room temperature. The reaction mixture thus obtained consisted of an oil phase and an aqueous phase. The aqueous phase containing a substantial portion of the nitric acid was removed and further processed to recover polybasic acids. The oil phase was washed with water until the water used for washing was colorless. The oil phase was then heated over a boiling water bath to drive off residual water. The product thus obtained was the water-insoluble nitrogen-containing product useful as an anti-rust agent according to our invention. The yield of product based on the weight of charge was 39.7 percent. The product had a neutralization number of 224, a saponification number of 437 and a molecular weight of 235. The oxidized product contained 55.52 percent carbon, 8.41 percent hydrogen, 6.29 percent nitrogen and 29.78 percent oxygen. The product was a non-viscous yellow liquid which had a rather pungent odor.

EXAMPLE 2

110.2 parts of a 132° F. melting point refined paraffin

wax was placed in a glass flask equipped with a stirrer and a reflux condenser. The wax was heated to 160° C. and maintained at that temperature for 12.8 hours during which period the wax was stirred and air was blown therethrough. The air-oxidized wax obtained from this treatment had a neutralization number of 96.9, a saponification number of 238 and a molecular weight of 486. The air-oxidized product contained 72.19 percent carbon, 10.66 percent hydrogen and 17.15 percent oxygen.

200 grams of the air-oxidized wax thus obtained and 1000 grams of 60 percent nitric acid were charged to a stainless steel rocking autoclave which was then sealed. The autoclave and contents were heated for a period of two hours to a maximum temperature of 120° C. during which time 148 grams of oxygen were metered into the autoclave. A maximum pressure of 500 pounds per square inch gauge was reached in this preparation. After the autoclave and contents had cooled to room temperature the contents were removed and treated in accordance with the separation and purification procedure described in Example 1. The oil phase which consisted of the water-insoluble nitrogen-containing product comprised 32.5 weight percent of the air-oxidized wax charge stock. The water-insoluble nitrogen-containing product had a neutralization number of 271, a saponification number of 345 and a molecular weight of 224. The product contained 67.59 percent carbon, 11.07 percent hydrogen, 0.9 percent nitrogen and 20.44 percent oxygen.

EXAMPLE 3

200 grams of air-oxidized wax having a saponification number of 238 obtained according to the procedure described in Example 2 and 1000 grams of 70 percent nitric acid were charged to a stainless steel rocking autoclave and further treated in accordance with the procedure described in Example 2. The yield of water-insoluble material obtained was 19.6 weight percent based on the charge of air-oxidized wax. The product thus obtained had a neutralization number of 730, a saponification number of 386 and a molecular weight of 205. The product contained 65.3 percent carbon, 10.5 percent hydrogen, 0.9 percent nitrogen and 23.3 percent oxygen.

In order to illustrate the improved anti-rust characteristics obtained in accordance with the invention a gasoline containing the water-insoluble nitrogen-containing reaction product obtained in Example 1, Example 2 and Example 3 has been compared with a gasoline containing no anti-rust agent, with a gasoline containing a commercially available anti-rust agent, and with a gasoline containing air-oxidized wax. The comparison was made by placing 6" x ¾" SAE 1020 sand blasted solvent rinsed steel strips in contact with mixtures of water and gasoline for prolonged periods of time. The steel strips were then examined for rust formation. In making the determinations, 400 ml. of gasoline and 100 ml. of distilled water were placed in a glass container. Steel strips were placed in the container so that part of the strip was in the water layer, another part in the gasoline layer, and a further part in the air space above the liquid. The container was tightly sealed and then violently agitated for about one minute. The container was then stored in the dark at room temperature without further agitation. Steel strips were removed from the container at different intervals to determine the amount of rust formed on the various segments. Steel specimens which were completely free from rust were given an anti-rust rating of 100. Steel strips which were completely covered with rust were given an anti-rust rating of zero.

Table I summarizes the results obtained with a regular grade leaded-gasoline containing the various additives in concentrations as shown.

Table I

Additive	Concentration, lb./1,000 bbl.	Anti-rust Rating, Time in Hours			
		0	24	142	162
None		100	44	38	35
Do		100	[1] 46	[2] 33	[3] 33
Commercial anti-rust A	10	100	85	70	70
Do	15	100	[1] 94	[2] 72	[3] 70
Product of Example 1	15	100	100	100	100
Product of Example 2	15	100	100	100	100
Product of Example 3	15	100	100	100	100

[1] 3 hours.
[2] 113 hours.
[3] 161 hours.

The improved results obtained in accordance with our invention are apparent from the summary of data in Table I. It will be noted that the base gasoline gave very little protection against rusting. However, the nitric acid oxidation product of Examples 1, 2 and 3 gave prolonged protection at a concentration of 15 pounds per thousand barrels of gasoline. The protection thus obtained was greater than that obtained with the commercially available additive in a concentration of 15 pounds per thousand barrels of gasoline.

While air-oxidized wax gives some improvement in anti-rust properties over the gasoline itself, the improvement obtained is not as great as that obtained with a nitric acid-oxidized wax. Table II summarizes the results obtained with a regular grade leaded-gasoline containing various amounts of air-oxidized wax as shown.

Table II

Additive	Concentration, lb./1,000 bbl.	Anti-rust Rating, Time in Hours			
		0	24	142	162
None		100	71	46	45
Air-oxidized wax	5	100	94	80	79
Do	15	100	93	77	76
Do	25	100	97	82	81

As evidenced by the data in Table II, the air-oxidized wax gave some improvement in the anti-rust rating. However, it will be noted that the steel specimens contained some rust within 24 hours as shown by ratings below 100. By comparing the data in Table I with the data in Table II, it will be observed that the nitric acid oxidation products of Examples 1, 2 and 3 gave greater protection against rusting than the air-oxidized wax reported in Table II. Even though the base gasoline reported in Table I gave a lower anti-rust rating than the gasoline reported in Table II, the gasoline containing the nitric acid oxidation products of Examples 1, 2 and 3 gave complete protection as evidenced by the ratings of 100.

The above test was repeated with a premium grade leaded-gasoline containing smaller amounts of the nitric acid oxidation products of Examples 1, 2 and 3. The results obtained are summarized in Table III as follows:

Table III

Additive	Concentration, lb./1,000 bbl.	Anti-rust Rating after 6 weeks
None		30
Commercial anti-rust A	15	70
Product of Example 1	2	100
Product of Example 2	5	100
Product of Example 3	5	93

The above data clearly illustrate the improved results obtained when the water-insoluble nitrogen-containing reaction product is employed in concentrations of 2 to 5 pounds per thousand barrels of gasoline.

The physical characteristics of gasoline are not substantially changed by the addition of the water-insoluble nitric acid oxidation product as evidenced by the following data.

Test	Gasoline	Gasoline +15 lb./1,000 bbl. Product of—		
		Example 1	Example 2	Example 3
Existent Gum, mg./100 ml.	2.7	3.7	3.2	3.2
Copper Dish Gum, ASTM D 910-52T, mg./100 ml.	22	25	26	24
Oxidation Stability, 212° F., min.	457	548	446	504
Copper Strip Test, 122° F., 3 hr.	Blank	Blank	Blank	Blank
Knock Rating:				
Research Method	92.0	91.9	92.0	92.0
Motor Method	83.2	83.1	83.1	82.8

It will be noted that the addition of the water-insoluble nitrogen-containing product has very little effect on the physical characteristics of the gasoline. While there appears to be a slight increase in the existent gum and in the copper dish gum, the increase is not actual gum formation but is due to the additive itself which being non-volatile, remains as a residue when the gasoline is evaporated.

In order to illustrate the effectiveness of the water-insoluble nitrogen-containing product of Example 1 in a slushing composition, accelerated tests were carried out in a humidity cabinet wherein SAE 1020 steel panels were subjected to saturated air conditions at a temperature of about 120° F. The particular test employed is that known as AN–H–31 humidity cabinet test. When steel panels coated with a 500/3 Texas oil were subjected to this test, rusting occurred within one hour. Steel panels coated with the same oil containing 3 percent by weight of the product of Example 1 did not rust for 69 days.

While our invention is described above with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such examples and embodiments and may be variously practiced within the scope of the claims hereinafter made.

We claim:

1. A hydrocarbon composition comprising a major amount of a liquid hydrocarbon normally tending to rust ferrous metals when contaminated with water and a small amount, sufficient to substantially retard such rusting, of the water-insoluble nitrogen-containing reaction product obtained by oxidizing at about 100° to about 400° C. one part by weight of a saturated aliphatic hydrocarbon boiling above about 250° F. and having at least 8 carbon atoms in the presence of about 2.5 to about 20 parts by weight of nitric acid having a concentration of at least about 50 percent.

2. A hydrocarbon composition comprising a major amount of a liquid hydrocarbon normally tending to rust ferrous metals when contaminated with water and a small amount, sufficient to substantially retard such rusting, of the water-insoluble nitrogen-containing reaction product obtained by oxidizing at about 100° to about 400° C. one part by weight of a saturated aliphatic hydrocarbon boiling above about 250° F. and having at least 8 carbon atoms in the presence of about 2.5 to about 20 parts by weight of nitric acid having a concentration of at least about 50 percent, the nitrogen content of said reaction product comprising about 0.5 to about 7.0 percent by weight of the reaction product.

3. A hydrocarbon composition having improved anti-rust characteristics which comprises a major amount of a liquid hydrocarbon containing about 1 to about 20 pounds per thousand barrels of liquid hydrocarbon of the water-insoluble nitrogen-containing reaction product obtained by oxidizing at about 100° to about 400° C. one part by weight of a petroleum wax in the presence of about 2.5 to about 20 parts by weight of nitric acid having a concentration of at least about 50 percent, the nitrogen content of said reaction product comprising about 0.5 to about 7.0 percent by weight of the reaction product.

4. A motor fuel having improved anti-rust characteristics which comprises a major amount of gasoline containing about 2 to about 15 pounds per thousand barrels of gasoline of the water-insoluble nitrogen-containing reaction product obtained by oxidizing at about 100° to about 400° C. one part by weight of a petroleum wax in the presence of about 2.5 to about 20 parts by weight of nitric acid having a concentration of at least about 50 percent, the nitrogen content of said reaction product comprising about 0.5 to about 7.0 percent by weight of the reaction product.

5. A motor fuel having improved anti-rust characteristics which comprises a major amount of gasoline containing about 2 to about 15 pounds per thousand barrels of gasoline of the water-insoluble nitrogen-containing reaction product obtained by oxidizing at about 100° to about 400° C. one part by weight of petroleum wax having a melting point of about 132° F. in the presence of about 2.5 to about 20 parts by weight of nitric acid having a concentration of at least about 50 percent, the nitrogen content of said reaction product comprising about 0.5 to about 7.0 percent by weight of the reaction product.

6. A slushing composition consisting essentially of a petroleum oil containing about 0.5 to about 10 percent by weight of the water-insoluble nitrogen-containing reaction product obtained by oxidizing at about 100° to about 400° C. one part by weight of a petroleum wax in the presence of nitric acid having a concentration of at least about 50 percent, the nitrogen content of said reaction product comprising about 0.5 to about 7.0 per cent by weight of the reaction product.

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