

UNITED STATES PATENT OFFICE

2,632,695

RUST INHIBITOR FOR LIGHT PETROLEUM PRODUCTS

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9 Claims. (Cl. 44-66)

1

The present invention relates to the prevention of the formation of rust on metallic surfaces in contact with mineral oil products and more particularly to prevention of a formation of rust on metallic surfaces in contact with mineral oil products such as gasoline, naphthas and burning oils.

The problem of preventing the formation of rust on metallic surfaces in contact with mineral oil products has received considerable attention in the past decade with respect to those fractions of mineral oil which are used for lubricating purposes. However, the prevention of the formation of rust on metallic surfaces in contact with what may be termed "light products," i. e., naphtha, including thereby gasoline and kerosene and burning oils, has not received so much consideration. While the problem may seem to be the same, nevertheless the problem of preventing the formation of rust on metallic surfaces in contact with naphthas and the like presents factors which are not encountered when confronted with the problem of preventing the formation of rust on metallic surfaces in contact with lubricating cuts of mineral oil.

One of the most important limitations upon the use of a rust preventive in gasoline, for example, is the limitation that the color of the product must be the same as that of the unprotected gasoline; i. e., the rust preventive must not cause a color change in the gasoline by reaction with the hydrocarbon constituents of the gasoline, dyes, components of tetraethyl lead fluid, anti-oxidants, etc., normally contained or added to gasolines. Furthermore, the rust inhibitor must be one which has no appreciable effect upon the octane rating or any of the other specifications under which the gasoline is sold.

Another factor which is of relatively no importance when considering the formulation of a lubricating oil is that of the effect of extreme pressures on the separation or other action of the rust preventive. Thus, for example, it is well known that products such as gasoline, kerosene and burning oils are in many instances transferred from the refinery to distributing points via pipe lines. Pressures as high as 1200 p. s. i. may be encountered in such pipe line transportation. Consequently, it is essential that the rust preventive remain with the petroleum cut regardless of the pressure to which the cut is subjected.

Another factor controlling the selection of a

2

rust preventive for mineral oil fractions, other than lubricating oil fractions, is the tendency of some known rust preventives to cause the formation of emulsions. Rust preventives which tend to emulsify the water present with the mineral oil fraction are not useful because they tend to hold unusually large amounts of water in the petroleum products.

Indicative of the problem presented in preventing the formation of rust on metallic surfaces in contact with gasoline, kerosene, burning oils and the like is the fact that of 51 materials tested, 50 failed to provide the protection required at concentrations commensurate with practical limitations. Of the 50 that failed, failure was due to a color change in the gasoline in 18 instances. Of the remaining 32, 7 failed because of their emulsifying action and the remainder failed to provide the required protection at practical concentrations. Thus, it is manifest that although a large amount of information has been obtained upon the solution of the problem of preventing the formation of rust on metallic surfaces in contact with lubricating fractions of mineral oil, nevertheless the problem of preventing the formation of rust on metallic surfaces in contact with naphthas, burning oils and the like still remains to be solved.

An important limitation upon the use of a rust preventive in gasoline is its effect upon gum formation. As a generalization, it can be said that rust preventives are non-volatile in nature, and increase the amount of gum formed by the amount of rust preventive added. Consequently, a rust preventive useful in gasoline is one which is effective in concentrations not more than about 0.008 weight per cent of non-volatile residue. Accordingly, it is an object of the present invention to provide a gasoline, kerosene or burning oil fraction of mineral oil containing an amount of rust preventive not substantially in excess of about 0.008 weight per cent non-volatile residue.

It has now been discovered that dimeric acids are compounds which satisfy all of the requirements of a rust preventive for naphthas and burning oils.

A dimer, as defined in Hackh's Chemical Dictionary, is a condensation product or polymer of two molecules. Thus, when two molecules of a polyethenoid mono-carboxylic fatty acid condense to form a di-carboxylic acid, the product by definition is a dimer, or the mono-carboxylic acid

is said to be dimerized. Similarly, the condensation of a molecule of one polyethenoid mono-carboxylic acid with a molecule of a second polyethenoid mono-carboxylic acid forms a dimer which is a di-carboxylic acid.

In general, the dimeric acids have been produced by heat polymerization of esters of the mono-carboxylic acids to esters of the dimeric acids followed by hydrolysis. The glycerides have also been heat polymerized and the product hydrolyzed to yield the free dimeric acids. Recently, Goebel in U. S. Patent No. 2,482,761 disclosed that the free fatty acids can be polymerized. Briefly, Goebel's process comprises preparing unsaturated fatty acids by hydrolyzing a fat or oil for example, soya bean fatty acids, adding a small portion of water, and heating in a pressure vessel until substantially all of the di- and tri-unsaturated fatty acids present polymerize. The resultant product can then be heated at reduced pressure, to distill off vaporizable constituents, which include mainly saturated acids and mono-unsaturated acids. A temperature of at least 260° C. must be used and preferably from 330° C. to 360° C. and a heating period of 3 to 8 hours to produce substantially complete polymerization of di- and tri-unsaturated material. Numerous catalysts can be employed but are not necessary. Among the catalysts which can be used are mercuric acetate, lead acetate, anthraquinone, and Raney nickel.

Thus, for example, as described in U. S. Patent No. 2,482,761, 300 parts by weight of sardine oil having an iodine value of 188 were pressure split with 600 parts of water at 260° C. Three treatments of 1½, ½ and ½ hour duration were used with 100 parts of the water employed in each treatment.

Water was withdrawn and the wet acids were heated to 350° C. at a pressure of 250 pounds per square inch for 4½ hours.

The product was then heated at reduced pressure to distill off unpolymersed material yielding 44% by weight of a residue having an iodine value of 86.3 and a neutralization equivalent of 386.

In a similar manner, as described in the aforesaid patent, linseed fatty acids, soya bean fatty acids and the fatty acids of other drying or semi-drying oils can be polymerized to produce what the patentee names dimeric acids. The patentee states that by his process larger yields of dimeric acids are formed and less of the trimeric and higher polymeric acids are formed.

Another source of dimeric acids is the still residue of the dry distillation of castor oil in the presence of sodium hydroxide. An analysis of the fatty acids from castor oil has been reported in Chem. Abs. 34, 3521³ as follows:

	Per cent
Ricinoleic acid.....	87
Oleic acid.....	7
Linoleic acid.....	3
Saturated acids.....	3

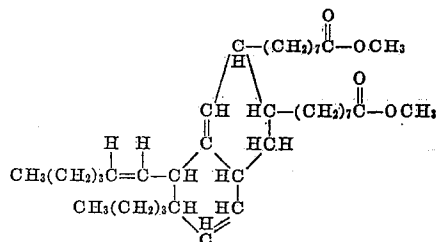
Distillation of the aforesaid still residue yields two approximately equal fractions, the distillate and a second still residue. The distillate is a mixture of undecylic, palmitic and stearic acids together with minor amounts of unsaturated mono-meric fatty acids. The second still residue is a mixture of which about 50% by weight is polymerized fatty acids having a molecular weight of 360 to about 600 and the balance a still residue having a molecular weight in excess of 600.

The material of the first still residue of the dry distillation of castor oil in the presence of sodium hydroxide has the following properties:

	Lot 1	Lot 2
Neutralization No.....	164	159.9
Bromine No.....	20.7	19.4
Kinematic Viscosity at 100° F.....	3096	1373
Lovibond color.....	>750	750
A. P. I. Gravity, degrees.....	14.6	15.2
Specific Gravity.....	0.9685	0.9646

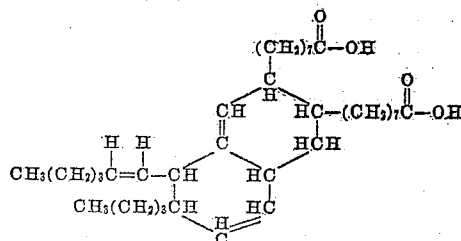
The dimeric acids on the basis of the present data are mono-cyclic or dicyclic hydroaromatic dicarboxylic acids depending upon the degree of unsaturation of the mono-carboxylic acids from which the dimeric acids are obtained. Thus, octadecadienoic acids polymerize to mono-cyclic hydroaromatic dicarboxylic acids while octadecatrienoic acids polymerize to bicyclic hydroaromatic dicarboxylic acids.

Thus, when conjugated and non-conjugated methyloctadecatrienates polymerize by bimolecular addition involving an additional intramolecular ring closure, a compound having the structure shown in Formula I, or isomers thereof, is formed:



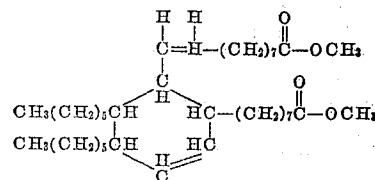
FORMULA I

This compound after hydrolysis yields the free acid having the structure shown in Formula II, or isomers thereof:



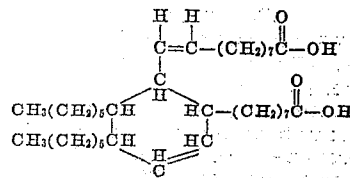
FORMULA II

The octadecadienate esters dimerize by 1,4-diene addition to a compound having the structure shown in III, or isomers of it.



FORMULA III

This dimer upon hydrolysis yields the free acid having the structure given in Formula IV, or isomers of it.



FORMULA IV

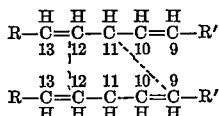
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When one of the free octadecadienoic or octadecatrienoic acids are polymerized as described in U. S. Patent No. 2,482,761, the patentee's dimeric acids have the structures shown in Formulas II and IV, or isomers of them.

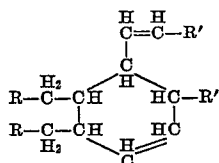
Castor oil contains ricinoleic acid in the form of a glyceride. The most important pyrolytic reaction of ricinoleic acid and its esters is that of dehydration to produce octadecadienoic acids. Therefore, in the dry distillation of castor oil in the presence of sodium hydroxide the higher boiling portion, i. e., the still residue is a mixture of polymerized octadecadienoic acid derived from the ricinoleic acid and the linoleic acid present in the castor oil.

From the foregoing a generic formula for the dimeric acids of the present invention can be written. Thus, as an example of an octadecadienoic acid, the polymerization of linoleic acid is illustrative. Linoleic acid or $\Delta^9,10,12,13$ -octadecadienoic acid is present in peanut, palm, olive, teaseed, kapok etc., oils in amounts of less than 25%. Oils such as corn germ, cottonseed, sunflowerseed, poppyseed, sesame, etc., contain 40% to 60% linoleic acid. The linoleic acid obtained from the great majority of plant sources is $\Delta^9,10,12,13$ -octadecadienoic acid.

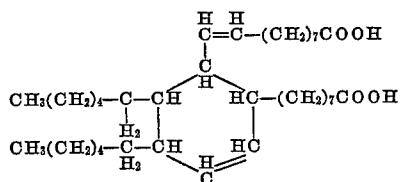
When $\Delta^9,10,12,13$ -octadecadienoic acid is dimerized in the absence of other polyethenoid acids, either as an ester or as the free acid in the manner described in U. S. Patent No. 2,482,761, a reaction which takes place can be illustrated by the following formula:



with a shift in the double bond this becomes:

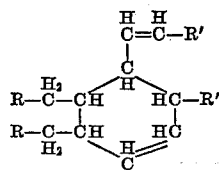


where $\text{R}=\text{CH}_3(\text{CH}_2)_4$ and $\text{R}'=(\text{CH}_2)_7\text{COOH}$. However, for the various isomers of linoleic acid R will have a different value. Thus artificial linoleic or octadecadienoic acids have their origin in three natural sources, (1) fatty acids more highly unsaturated than linoleic acid, which on partial hydrogenation form isomeric acids, (2) normal linoleic acid whose double bonds may be shifted by isomerization catalysts and (3) monoethenoid hydroxy acids, such as ricinoleic acid, which on dehydration form an additional double bond. For example, ricinoleic acid dehydrates to two isomeric linoleic acids, $\Delta^9,10,11,12$ -octadecadienoic acid and $\Delta^9,10,12,13$ -octadecadienoic acid. When $\Delta^9,10,11,12$ -octadecadienoic acid dimerizes in the absence of other polyethenoid acids, the resulting dimeric dicarboxylic acid has the formula

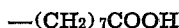


or

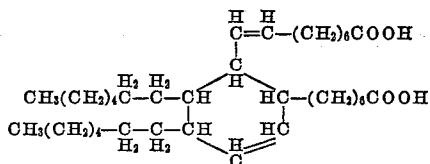
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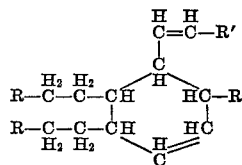
where R is $\text{CH}_3(\text{CH}_2)_4$ — and R' is



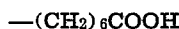
However, when the monocarboxylic acid is $\Delta^8,9,12,13$ -isomer the dimeric dicarboxylic acid has the structure



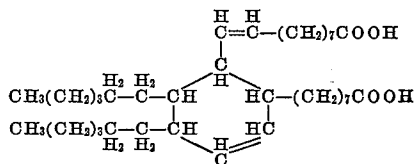
or,



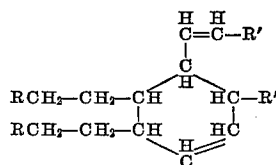
where R is $-\text{CH}_3(\text{CH}_2)_4$ and R' is



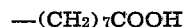
Similarly with the $\Delta^9,10,13,14$ -isomer the dimeric dicarboxylic acid has the structure



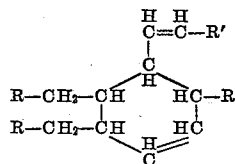
or,



where R is $\text{CH}_3(\text{CH}_2)_3$ and R' is $-(\text{CH}_2)_7\text{COOH}$. It follows that when the $\Delta^9,10,12,13$ -isomer is dimerized R is $\text{CH}_3(\text{CH}_2)_4$ — and R' is



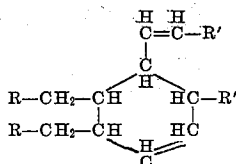
when the $\Delta^9,10,11,12$ -isomer is dimerized R is $\text{CH}_3(\text{CH}_2)_4$ — and R' is $-(\text{CH}_2)_7\text{COOH}$; when the $\Delta^8,9,12,13$ -isomer is dimerized R is $-\text{CH}_3(\text{CH}_2)_5$ — and R' is $-(\text{CH}_2)_6\text{COOH}$; and when the $\Delta^9,10,13,14$ -isomer is dimerized R is $-\text{CH}_3(\text{CH}_2)_4$ — and R' is $(\text{CH}_2)_7\text{COOH}$. For these 4 isomeric linoleic acids the generic structure for the dimeric acid can be written



where R is $\text{CH}_3(\text{CH}_2)_4$ — for the $\Delta^9,10,12,13$ -isomer and the $\Delta^9,10,11,12$ -isomer, and $\text{CH}_3(\text{CH}_2)_5$ — for the $\Delta^8,9,12,13$ - and $\Delta^9,10,13,14$ -isomer, R' is

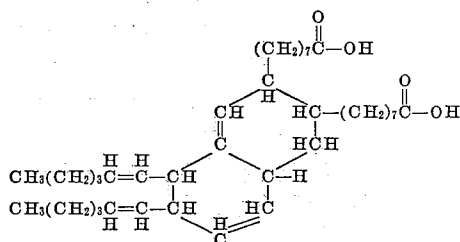
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—(CH₂)₇COOH for the Δ_{9,10,12,13}-, Δ_{9,10,11,12}- and Δ_{9,10,13,14}-isomers and (CH₂)₆COOH for the Δ_{8,9,12,13}-isomer, it becomes obvious that in the generic formula for the dimeric acids derived from the individual diethenoid monocarboxylic acids R will have a significance of CH₃(CH₂)_n— where *n* is one more than the number of CH₂— groups between the terminal CH₃ group and the nearer carbon of the nearer double bond and R' will have the significance (CH₂)_mCOOH in which *m* is the number of CH₂— groups between the carboxylic groups of the monocarboxylic acid and the nearer carbon of the nearer double bond. From this it follows that the generic formula for dimeric acids derived from a single di-ethenoid 15 monocarboxylic aliphatic acids is

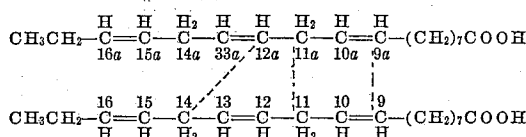


where R is CH₃(CH₂)_n— and R' is (CH₂)_mCOOH and *n* and *m* have the values given hereinbefore.

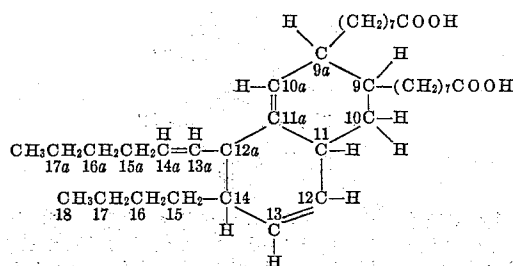
When polyethenoid acids, i. e., tri- and greater ethenoid acids such as *n*-linolenic acids are dimerized, the dimeric acids obtained are bicyclic dicarboxylic acids having the formula



when only a single acid undergoes polymerization. Typical of the triethenoid acids are linolenic or Δ_{9,10,12,13,15,16}-octadecatrienoic acid and elaeostearic or Δ_{9,10,11,12,13,14}-octadecatrienoic acid. When Δ_{9,10,12,13,15,16}-octadecatrienoic acid is the sole polyethenoid acid present it polymerizes to form the dimeric dicarboxylic acid the condensation can be pictured as occurring as follows:

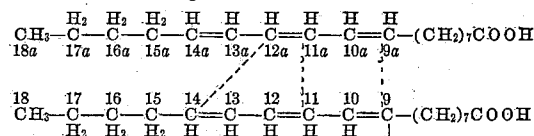


with a shift of the double bonds at 15 and 16 the formula of the dimeric acid becomes:

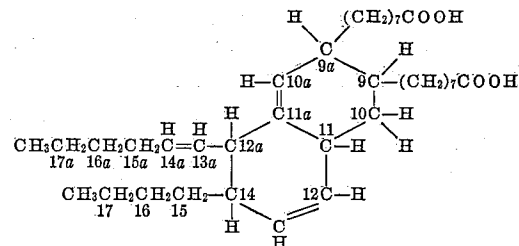


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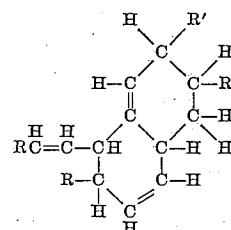
When Δ_{9,10,11,12,13,14}-octadecatrienoic acid is the sole acid polymerized to form the dimeric dicarboxylic acid the condensation can be pictured as occurring as follows:



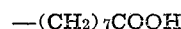
which the shift of the double bond at 11a and 11 becomes



The generic formula for the dimeric dicarboxylic acids derived from the dimerization of individual triethenoid octadecatrienoic acids is



where R is CH₃(CH₂)₃— and R' is



A well known source of these dimeric acids is the product sold by Emery Industries, Inc., and said to be dilinoleic acid. In the literature published by the Emery Industries, Inc. the properties of this product are given as follows:

Neutral equivalent	290-310
Iodine value	80-95
Color	Gardner 12 (max.)
Dimer content	Approx. 85%
Trimer and higher	Approx. 12%
Monomer	Approx. 3%

Tests of several batches of material supplied by this producer indicate that the properties of this product are within the limits set forth hereinafter:

Specific gravity, ° A. P. I.	15-15.1
Specific gravity, D60/60	0.9665
Color, Lovibond	35
Kinematic viscosity @ 100° F., centistokes	2462-2666
A. S. T. M. bromine No.	39.3
Neutrality No.	186.8-190.4
Iodine value	67-86

It will be noted that the dimeric acids available from the Emery Industries, Inc., contain approximately 85% dimeric acids and about 12% trimeric and higher polymeric acids and the second still residue of the dry distillation of castor oil in the presence of sodium hydroxide contains about 45-50% of the dimeric acids and about 50% of the trimeric and higher polymeric acids.

Since neither of these industrially available prod-

ucts is 100% dimeric acids it is manifest that materials containing more highly polymerized acids than the dimeric acids can be used. However, it is to be noted that these materials contain only small amounts, say less than 10% of the monocarboxylic or unpolymerized fatty acids and saturated acids.

Accordingly, preferred materials are those containing not more than about 15% of unpolymerized unsaturated fatty acids and saturated fatty acids. In general, the content of dimeric acids and trimeric and higher acids should be of the order of at least about 85% with the dimeric acids representing at least about 50% of the dimeric and higher polymeric acids. Thus, the Emery Industries dimeric acids contain about 85% dimeric acids while the second still residue of the dry distillation of castor oil in the presence of sodium hydroxide contains about 46.8% dimeric acids. Those skilled in the art will recognize that the lower the concentration of dimeric and higher polymeric acids the greater the amount of the mixture required to provide the protection against the formation of rust. Consequently, a point will be reached at which the concentration of non-polymeric acids will be sufficiently low to require the use of such an amount of the mixture containing the polymeric acids that the non-volatile residue left in gasoline for example will exceed that permitted by the specifications. Accordingly, the concentration of dimeric and higher polymeric acids in a mixture should be high enough that effective protection against the formation of rust is obtained but the non-volatile residue of the protected petroleum fraction does not exceed that permitted by the specifications.

The efficacy of dimeric acids as a rust-preventive in gasoline, naphthas and burning oils was determined by three tests. One was the modified A. S. T. M. D665-47T test, which has been stated to be more severe in many respects than actual pipe line conditions in that it is run at a higher temperature (80° F.) than is usually found in a pipe line, with a much higher relative amount of water present and under conditions such that the test materials are saturated with oxygen at all times. It has been said that test specimens exposed to the severe rusting conditions of this test for two days are rusted to substantially the same degree as those exposed in a products pipe line for 30 to 60 days. The A. S. T. M. test was modified to the extent of lowering the test temperature from 140° F. to 80° F. for 48 hours and employing distilled water.

When samples of finished gasoline containing normal amounts of dye, tetraethyl lead, anti-oxidants, etc., and the indicated amounts of dilinoleic acid were subjected to the aforesaid A. S. T. M. test, the following results were observed:

Light Product	Concentration of Dimeric Acids (Percent Weight)	A. S. T. M. Test Results
Gasoline.....	0.0053	Pass.
Do.....	0.0032	Do.
Do.....	0.0022	Do.
Do.....	0.0011	Do.
Do.....	0.0011	Do.
Do.....	0.0011	Do.
Kerosine.....	0.0010	Do.
Middle Distillates.....	0.0010	Do.
Gasoline.....	0.0009	Do.
Do.....	0.0009	Do.
Do.....	0.0006	Do.
Do.....	0.0006	Fail.
Do.....	0.0004	Do.

It is to be understood that all evaluations were made in sets of ten samples, one sample being an uninhibited petroleum fraction control blank which failed in all cases. The test was only rated as passing when the test specimen in fractions boiling above gasoline showed no rust below or above the interface after the test period.

However, when testing protected gasoline and other light products, no significance was placed on the appearance of several rust spots above the interface of the test coupon. Evaporation of the sample and spraying of the sample with water above the level of the liquid being tested was unavoidable. Consequently, rust on the unprotected part, i. e., the area above the oil surface of the coupon, has little meaning.

The rust preventive was also subjected to a static rust test. The static rust test has been described by Baker, Jones and Zisman, IEC 41, 137 (1949). In this test a steel plate cut in the shape of an equilateral triangle and pressed to form a shallow cup in the center is immersed in the test oil. After standing in the test oil for one hour in 100° F., a droplet of distilled water is placed on the center of the metal specimen and the test continued until visual rust appears on the metal surface. In this test the dimeric acids were the most effective of all materials tested in concentrations of 0.0011 to 0.0053 weight per cent.

To determine the effect of pressure upon the rust-preventing efficacy of the dimeric acids, a modification of the A. S. T. M. rust test was used. This test was carried out as follows: a rust-proof alloy pressure bomb equipped with a rocker arm for agitation was used. A. S. T. M. steel test coupons, fastened to the bomb head thermowell, were used. Pressure was obtained by injection of mixtures of nitrogen and oxygen gas as indicated in the following table:

Additive	Pressure, p. s. i. a.	Temp., °F.	Time of Test, Hours	Added Distilled Water, Percent Volume	Remarks
Uninhibited.....	{O ₂ Total 1. 15 1,200.....	80.....	48.....	10.....	Slight rust.
Do.....	165 1,200.....	80.....	48.....	20.....	Do.
0.0011 percent dimeric acids.....	15 1,200.....	80.....	48.....	20.....	No rust.
Do.....	165 1,200.....	80.....	48.....	20.....	Do.
0.0022 percent dimeric acids.....	15 1,200.....	80.....	48.....	None.....	Heavily mill scaled coupon used. ²

¹ Total pressure attained by adding nitrogen.

² No apparent change in amount of mill scale. Coupon weight before test, 93.3419 gm.; coupon weight after test, 93.3429 gm.

It is to be noted that the addition of the dimeric acids did not noticeably affect the A. S. T. M. boiling range, color or octane ratings, both motor and research method of finished gasoline as the following tabulation makes manifest.

Effect of dimer acids on properties of finished gasoline

	Concentration of Additive		
	None	0.0011 wt. percent	0.0053 wt. percent
Dist., A. S. T. M., °F.:			
IBP.....	95	94	95
5%.....	121	121	121
10%.....	138	137	137
20%.....	167	164	166
30%.....	191	191	191
40%.....	214	213	212
50%.....	231	231	230
60%.....	252	250	250
70%.....	273	270	272
80%.....	299	298	298
90%.....	339	335	338
EP.....	409	403	405
Rec., percent.....	96.5	96.5	96.5
Res., percent.....	1.2	1.2	1.2
Loss, percent.....	2.3	2.3	2.3
Color.....		(¹)	(¹)
Glass Dish Gum, mg./100 cc.....	1.6	1.7	4.4
Octane Rating: ²			
Motor method base.....	71.7	71.6	71.7
+1.0 cc. TEL/gal.....	77.9	77.8	78.4
+3.0 cc. TEL/gal.....	83.0	82.9	82.6
Research method base.....	74.0	74.0	74.0
+1.0 cc. TEL/gal.....	82.1	82.0	82.0
+3.0 cc. TEL/gal.....	87.5	87.2	87.4

¹ No noticeable change.

² Finished blend except for TEL.

When the dimeric acids are added to kerosene, the addition had no effect upon the A. S. T. M. boiling range, color, color stability, corrosion, flash, sulfur, B. S. & W., smoke point, or burning quality as the following tabulation clearly establishes:

Similarly, the addition of the dimeric acids to No. 2 fuel oil did not affect the gravity, A. S. T. M. boiling range, aniline cloud point, diesel index, flash, pour point, sulfur, corrosion, carbon residue, B. S. & W., ash or the factors of the fuel oil stability test, as is manifest upon study of the following tabulation:

Effect of dimer acids on properties of No. 2 fuel oil

	Concentration of Additive		
	None	0.0011 wt. percent	0.0053 wt. percent
Dimeric Acids.....			
Gravity ° A. P. I.....	36.3	36.3	36.3
Dist., A. S. T. M., ° F.:			
IBP.....	354	346	346
5%.....	407	407	405
10%.....	422	424	425
20%.....	447	446	447
30%.....	466	465	465
40%.....	484	483	483
50%.....	500	501	500
60%.....	518	518	516
70%.....	536	537	535
80%.....	560	561	558
90%.....	589	589	587
EP.....	637	639	636
Rec., Percent.....	98.5	98.5	98.5
Res., percent.....	1.5	1.5	1.5
Aniline Cloud Point.....	141	142	142
Diesel Index.....	51	51	51
Flash, Tag, ° F.....	150	150	147
Flash, PM, ° F.....	172	175	175
Pour, ° F.....	5	5	0
Sulfur, percent wt.....	0.50	0.51	0.55
Copper Strip Corrosion, 3 hrs. at 212° F.....	Passing	Passing	Passing
Carbon Residue (on 10% Bott.), percent wt.....	0.10	0.07	0.10
Ash, percent wt.....	Nil	Nil	Nil

Effect of dimer acids on properties of kerosene

Dimeric Acids.....	Concentration of Additive		
	None	0.0011 wt. percent	0.0053 wt. percent
Gravity, ° A. P. I.....	44.8	45.0	44.9
Dist., A. S. T. M., ° F.:			
IBP.....	331	335	335
5%.....	371	368	369
10%.....	378	378	379
20%.....	391	388	392
30%.....	404	399	402
40%.....	412	409	411
50%.....	421	419	420
60%.....	430	428	429
70%.....	442	440	441
80%.....	459	457	455
90%.....	479	477	476
EP.....	513	514	514
Rec., percent.....	98.5	98.5	98.5
Res., percent.....	1.4	1.4	1.4
Loss, percent.....	0.1	0.1	0.1
Color, Saybolt.....	+21	+21	+20
S/V Catalytic Color Stability.....	Good	Good	Good
Flash, Tag, ° F.....	116	116	115
Sulfur, percent wt.....	0.045	0.047	0.043
Copper Strip Corrosion, 3 hrs. at 212° F.....	Pass	Pass	Pass
B. S. & W., percent wt.....	Nil	Nil	Nil
Smoke Point, mm.....	28	28	28
Burning Quality:			
24 Hour Burn—			
Chimney.....	Light White	Light White	Light White
Wick Incrustation.....	Hard Granular	Hard Gran.	Hard Gran.
Deposit.....	Light Even	Heavy, Fairly even	Heavy, Fairly even
Mushroom.....	None	None	None
Flame Shape.....	Good	Good	Good
48 Hour Burn—			
Chimney.....	Dirty White	Heavy White	Heavy White
Wick Incrustation.....	Hard Granular	Hard Gran.; Slight Gloss	Hard Gran.; Slight Gloss
Deposit.....	Heavy Uneven	Heavy Uneven; Tend to lump	Heavy Uneven; Tend to lump
Mushroom.....	None	None	None
Fibre.....	Weakened	Weakened	Weakened
Char.....	1/4	1/4	1/4
Flame Shape.....	Held shape well	Held shape well	Held shape well
Change, ht.....	-1/8	-1/8	-1/8
Change, wth.....	-1/8	-1/8	-1/8
Oil Consumed, cc. hour.....	50.8	51.3	50.7

	Concentration of Additive		
	None	0.0011 wt. percent	0.0053 wt. percent
Dimeric Acids.....			
B. S. & W., percent wt.	Trace	Trace	Trace.
TSD Fuel Oil Stability Test:			
Test before aging—			
Color, NPA.....	2½—	2½—	2½—
600° Gum.....	7.9—	8.2—	7.7—
Test after aging—			
Color, NPA.....	3½—	3½—	3½—
600° Gum.....	6.9—	6.6—	7.4—
Insoluble, mg./100 ml.—			
Sed.....	4.3—	4.4—	4.6—
Insol. Gum.....	0.6—	0.4—	0.3—

The residue from a dry distillation of castor oil

	Neutraliza- tion Number	Bromine Number
5 Castor Oil Polymer Acids:		
Fraction 1.....	241.7	28.5
Fraction 2.....	159.6	17.6
Fraction 3.....	182.3	21.2
Fraction 4.....		
Residue.....	139.4	20.4
Emery Industries Dimer Acids:		
Fraction 1.....	175.0	44.1
Fraction 2.....	189.8	40.0
Fraction 3.....	186.5	36.5
Residue.....	153.6	30.4

These materials were subjected to the A. S. T. M. rust test at 80° F. and the following data obtained:

Rust Inhibiting Material	Calcu- lated Molec- ular Weight	Concentration in Finished Gasoline		
		0.001%	0.002%	0.004%
Emery Industries Dimer Acids.....		pass.....		
Castor Oil Polymer Acids:				
Lot 1.....		do.....		
Lot 2.....		do.....		
Emery Industries Dimer Acids:				
Fraction 1.....	450	do.....	pass.....	
Fraction 2.....	540	(50 pin pts. rust)	do.....	
Fraction 3.....	690	(12 pin pts. rust)	do.....	
Residue.....	>700	pass.....		
Castor Oil Polymer Acids:				
Fraction 1.....	360	(fail ¹ Lt. rust ²)	pass.....	pass.
Fraction 2.....	435	pass.....	do.....	Do.
Fraction 3.....	520	do.....	do.....	Do.
Fraction 4.....				
Residue.....	>600	pass.....	pass.....	pass.

¹ Uninhibited finished gasoline shows severe rust in this test.

² As defined hereinbefore, column 10, lines 17-23.

in the presence of sodium hydroxide was subjected to distillation in a molecular still and the following data obtained:

TABLE I

Fraction Number	B. P., ° C.	Pressure, millimeters of Mercury	Weight percent	Calculated ¹ Molecular weight
1.....	110-150	0.015	8.8	360
2.....	150-190	0.013	23.6	435
3.....	190-220	0.015	14.4	520
4.....	220-225	0.025	3.2	
Residue.....			50.0	>600

¹ Molecular weights were extrapolated from molecular still distillation temperatures. Analytical boiling point elevation methods of determining molecular weight yielded unusually high molecular weight values indicating molecular association.

² Predominately dimeric acids.

³ Predominately trimeric acids.

⁴ More than.

Emery Industries dimer acids when subjected to distillation in a molecular still yielded the following data:

Fraction Number	B. P., ° C.	Pressure, millimeters of Mercury	Weight percent	Calculated ¹ Molecular weight
1.....	160-200	0.020	33.7	450
2.....	200-240	0.020	54.2	540
3.....	240-290	0.020	7.2	690
Residue.....			4.9	>700

¹ See footnote to previous tabulation.

² Predominately dimeric acids.

³ Predominately trimeric acids.

⁴ Trimeric acids and higher.

⁵ More than.

It has been established hereinbefore that the addition of about 0.0006 to about 0.008 weight per cent of dimerized fatty acids; i. e., dimer acids to petroleum oil fractions other than lubricating fractions inhibited the formation of rust on ferrous metal containers in contact with so-protected petroleum oil fractions. This is rather surprising when it is considered that a turbine oil containing six times the maximum amount of dimer acids which it is now proposed be added to non-lubricating fractions failed to provide any protection. This is established by the following data:

[Base oil—turbine oil]

	A. S. T. M. D-665-47T Rust Test (140° F.)	
	Distilled Water	Synthetic Sea Water
Base oil.....	Fail—Heavy rust.	Fail—Severe rust.
Base oil + 0.05 wt. per- cent dimer acids.	do.....	Fail—Very heavy rust.

Indicative that “dimerized” fatty acids are unique in the field of application of the present invention is the fact that undimerized fatty acids fail to prevent the formation of rust in the modified A. S. T. M. test whereby the efficacy of dimerized fatty acids was determined. This is

manifest after study of the data presented in the following tabulation:

Petroleum Fraction	Additive*	Conc., Percent Weight	Modified ¹ A. S. T. M. Test
Finished Gasoline	(A)-----	0.0074	Fall.
	A-----	0.0015	Do.
	B-----	0.0074	Do.
	(B)-----	0.0015	Do.
	C-----	0.0074	Do.
	(C)-----	0.0015	Do.
	D-----	0.0011	Pass.
	(D) A-----	0.0011	Pass.

*D. A.—dimerized fatty acids.

A—mixture of undimerized fatty acids: 53 percent linoleic acid, 34 percent oleic acid, 2 percent linolenic acid and 11 percent saturated acids.

B—mixture of undimerized fatty acids: 40 percent linoleic acid, 50 percent oleic acid, 4 percent linolenic acid and 6 percent resin acid.

C—mixture of C₁₂ to C₂₂ aliphatic monocarboxylic acids, about 50 percent saturated acids and the balance unsaturated acids.

¹ Modified A. S. T. M. D-665-47T, distilled water, 48 hours @ 80° F.

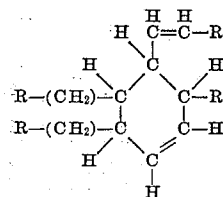
The dimerized fatty acids are unique in another characteristic; i. e., failure in the A. S. T. M. rust test for turbine oils (using distilled water) at concentrations much higher than the maximum permitted in gasoline for example. Thus, while dimerized fatty acids give satisfactory protection in gasoline, naphtha, fuel oil and like fractions of petroleum other than lubricating oil fractions in concentrations as low as 0.001 weight per cent, when subjected to the A. S. T. M. test for turbine oil protection at 140° F. dimerized fatty acids fail even in concentrations as high as 5 weight per cent.

The foregoing discussion provides a basis for stating that the present invention provides a means of inhibiting the rusting of ferrous metals in contact with non-lubricating fractions of mineral oil by incorporating an amount of dimerized fatty acids, designated by Goebel in U. S. Patent No. 2,482,761 at column 7, lines 8 to 20 as dimeric acids, in non-lubricating fractions of mineral oil effective to inhibit rusting of ferrous metals with which the mixture is in contact. The rusting of pipe lines and storage vessels fabricated from ferrous metals is inhibited when the non-lubricating fraction of mineral oil containing an effective amount of dimeric acids is transported or stored in such containers.

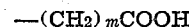
The dimeric acids can be characterized as being dicarboxylic acids having either one substituted six-membered hydroaromatic ring or having two fused six-membered hydroaromatic rings the one of which does not carry the two carboxylic acid groups being disubstituted. The dimeric acids are further characterized by having the two carboxylic acid groups attached to a single six-membered hydroaromatic ring through a plurality of (CH₂)— groups the number of such groups being dependent upon the number of such groups between the carbon atom of the carboxylic acid group and the nearer carbon of the nearest double bond of the monocarboxylic acid. The substituents are alkyl or alkenyl groups depending upon the degree of unsaturation of the monocarboxylic acid from which the dimeric acid is derived. Thus, the dimeric acids derived from a diethenoid fatty acid, or a dienoid acid have a single six-membered hydroaromatic ring substituted in two immediately adjacent positions by two alkyl groups and in two other immediately adjacent positions by carboxylic acid groups separated from the hydroaromatic ring in one substituent by a straight chain unsaturated aliphatic group and in the other by a straight chain saturated aliphatic

group. Consequently, the dimeric acids of the rust inhibiting material when prepared from the individual monocarboxylic acid are represented by two formulae

(1)

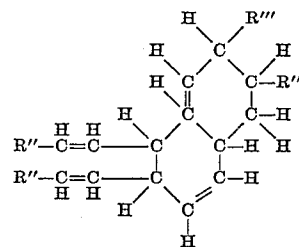


15 where R is CH₃(CH₂)_n—, and R' is

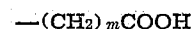


and n is a small number one more than the number of CH₂= groups between the terminal CH₃— group and the nearer carbon of the nearer double bond of the diethenoid monocarboxylic acid from which the dimeric acid is derived and m is a small number representing the number of CH₂= groups between the carbon of the carboxylic group and the nearer carbon of the nearer double bond of the diethenoid monocarboxylic acid from which the dimeric acid is derived, and

(2)



40 where R'' is CH₃(CH₂)_n and R''' is



and n and m have the same significance as before.

It follows that the present invention is the provision of a new composition of matter comprising a normally liquid non-lubricating fraction of mineral oil containing an amount of dimeric acids effective to inhibit rusting of ferrous metals with which said composition is in contact. The dimeric acids are dicarboxylic acids selected from the group consisting of (1) dicarboxylic acids having one six-membered hydroaromatic ring having two alkyl groups in immediately adjacent positions and two carboxyl groups one of which is attached to said hydroaromatic ring through a straight chain unsaturated aliphatic group having the double bond adjacent to said ring and the other carboxyl group being attached to said ring through a straight chain saturated aliphatic group and (2) dicarboxylic acids having two fused six-membered hydroaromatic rings to one of which are attached two straight chain unsaturated aliphatic groups in immediately adjacent positions and to the other ring two carboxylic acid groups are attached in immediately adjacent positions through two straight chain aliphatic groups. The dimeric acids are dicarboxylic acids derived from two molecules of polyethenoid fatty acids of drying and semi-drying oils and from fatty acids such as ricinoleic acid which upon dehydration become polyethenoid fatty acids. Therefore, in general, dimeric acids are dicarboxylic acids derived by the condensation of two

molecules one or more polyethenoid aliphatic monocarboxylic acid.

While the dimeric acids can be used in pure form, for practical reasons impure forms are used. That is to say, the dimeric acids are not presently available at commercially attractive costs in pure form. The purest form examined contained about 85% dimeric acids—the impurest sample examined contained about 45% dimeric acids. Accordingly, it is to be understood that in the data presented hereinbefore the concentrations of dimeric acids given therein are values based upon the impure dimeric acids uncorrected for concentration of dimeric acids present in the mixture. Thus, the addition of 0.001% of either Emery Industries Inc. dimer acids or castor oil polymer acids were equally effective although the castor oil polymer acids contained only about 45% dimeric acids and the balance higher polymeric acids while the Emery Industries Inc. dimer acids contained about 85% dimeric acids and about 12% higher polymeric acids.

While the structural formulae can be written for the dimeric acids produced when only one polyethenoid aliphatic monocarboxylic acid is present in the mixture undergoing polymerization, it is manifest that a generic structural formula cannot be written for the dimeric acids produced when a mixture of polyethenoid aliphatic monocarboxylic acids is polymerized. This is self-evident from a consideration of the previous discussion of the effect of the positions of the double bonds of the monocarboxylic acid upon the length of the substituent groups. Accordingly, the rust inhibiting material of the present invention is defined simply as dimeric acids in accordance with Goebel's usage in U. S. Patent No. 2,482,761 or as dimeric acids produced by the condensation of two molecules of polyethenoid aliphatic monocarboxylic acids.

This application is a continuation-in-part of co-pending application, Serial No. 125,844, filed November 5, 1949, now abandoned.

We claim:

1. A normally liquid, non-lubricating mineral oil fraction containing a minor proportion, sufficient to prevent rusting of ferrous metal surfaces in contact therewith, of an antirust agent selected from the group consisting of (1) dimeric acids produced by the condensation of unsaturated, aliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (2) dimeric acids produced by the condensation of hydroxyaliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (3) trimeric acids produced by the condensation of unsaturated, aliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (4) trimeric acids produced by the condensation of hydroxyaliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule.

2. A normally liquid, non-lubricating mineral

oil fraction containing between about 0.0006 per cent and about 0.008 per cent, by weight, of an antirust agent selected from the group consisting of (1) dimeric acids produced by the condensation of unsaturated, aliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (2) dimeric acids produced by the condensation of hydroxyaliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (3) trimeric acids produced by the condensation of unsaturated, aliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (4) trimeric acids produced by the condensation of hydroxyaliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule.

3. A normally liquid, non-lubricating fraction of mineral oil containing between about 0.0006 per cent and about 0.008 per cent, by weight, of essentially dimerized linseed oil fatty acids having the following characteristics:

Neutral equivalent	290-310
Iodine value	80-95
Dimeric acid	Approx. 85%
Trimeric acid and higher polymers	Approx. 12%
Monomeric acid	Approx. 3%

4. A normally liquid, non-lubricating fraction of mineral oil containing between about 0.0006 per cent and about 0.008 per cent, by weight, of essentially dimerized castor oil fatty acids having the following characteristics:

Neutralization No.	159-164
Bromine No.	19-21
Dimeric acid	About 45-50%
Trimeric acid and higher polymers	Balance

5. A composition as defined in claim 3 wherein the normally liquid, non-lubricating fraction of mineral oil is kerosene.

6. A composition as defined in claim 3 wherein the normally liquid, non-lubricating fraction of mineral oil is a distillate fuel oil.

7. A composition as defined in claim 3 wherein the normally liquid, non-lubricating fraction of mineral oil is gasoline.

8. A composition as defined in claim 4 wherein the normally liquid, non-lubricating fraction of mineral oil is a distillate fuel oil.

9. A composition as defined in claim 4 wherein the normally liquid, non-lubricating fraction of mineral oil is gasoline.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
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