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RUST PREVENTIVE COMPOSITIONS CONTAINING HETEROCYCLIC KETONE CONDENSATES OF ACYCLIC SUCCINIC ACIDS

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8 Claims. (Cl. 252—51.5)

The present invention relates to new compositions of matter and also to mineral oil compositions containing the new products. The compositions comprising the present invention are formed by the reaction, as later set forth in specific examples, of an alkyl or alkenyl succinic acid or anhydride wherein the alkyl or alkenyl group contains from 8 to 15 carbon atoms with a heterocyclic keto compound, for example a lactam such as gamma-butyrolactam (2-pyrrolidinone), gamma-valerolactam (5-methyl-2-pyrrolidinone), N-methyl pyrrolidinone, 2-piperidone, 3-methyl 2-piperidone, 3-ethyl 2-piperidone, 3-propyl 2-piperidone, oxindole and dioxindole, or a lactone, as for example butyrolactone. The new compositions are oil soluble, particularly in petroleum oil fractions, and have been found to exhibit rust preventive properties towards metals, especially steel and ferrous iron surfaces. The simplest and most convenient method of developing a rust preventing film on a metal surface is to dissolve one of the preferred class of rust preventive compounds disclosed herein in a suitable petroleum base carrier such as a motor gasoline, aviation gasoline, jet fuel, turbine oil and the like. Inasmuch as the lead salts of compounds of the herein preferred class of compounds do not form, or if formed are completely soluble in the petroleum fraction employed, the compounds hereinafter described may be used in tetraethyl lead treated fuels. Moreover, the alkaline earth salts of the preferred class of compounds either do not form when contacted with sea water or are soluble in hydrocarbons, thereby permitting the use of sea water balast in storage tanks earlier loaded with an oil fraction or fuel treated with one of the preferred rust preventive compounds.

Since the structure of the new compounds is not known with certainty, they can be described only as reaction products but the invention can be readily understood from the description that follows as examples of the formation of the compounds and their use as rust preventives.

EXAMPLE 1.—PRODUCT A

Into a vessel provided with a stirrer, condenser and temperature recording means, there were added 131.5 parts of dodecenyl succinic anhydride and 42.5 parts of 2-pyrrolidinone (gamma-butyrolactam). The anhydride was obtained from propylene polymer and maleic anhydride and may also be called tetrapropenyl succinic anhydride. The agitated mixture was then heated between 110–116° C. for a period of several hours and the neutralization number determined from time to time on samples withdrawn from the reaction. Since there was no change in this value for a 5 hour period, the heating was discontinued after an overall heating time of 8½ hours to obtain a product with a neutralization number of 236. The course of the reaction is unknown but probably involves splitting both the lactam and anhydride rings to form an amide. However, a neutralization number of 320 is the calculated value for the mixed anhydride amide which would be formed by splitting the 2-pyrrolidinone ring between the nitrogen and the carbonyl, the nitrogen forming an amide and the carbonyl reforming an anhydride linkage by uniting with the acid radical liberated from the succinic anhydride. The product was completely soluble in concentrations of 1% and 5% in petroleum ether and formed bright solutions in both instances.

EXAMPLE 2.—PRODUCT B

Into the same type equipment employed in Example 1, there were added 131.5 parts (0.5 mole) of dodecenyl succinic anhydride, 9 parts (0.5 mole) of water and 49.6 parts (0.5 mole) of N-methyl 2-pyrrolidinone. The agitated mixture was heated at 98–102° C. and samples withdrawn from time to time and tested to determine the neutralization number. Titration with alcoholic caustic potash should develop a value of 290 for complete reaction. Heating of the mixture was discontinued after 10⅓ hours since the neutralization number appeared to be constant at 278. The product of the reaction was completely soluble in petroleum ether.

EXAMPLE 3.—PRODUCT C

Example 1 above was duplicated except that 9 parts of water were added to the original charge and heating carried out at 95–98° C. for 4¾ hours. A product possessing a neutralization number of 286 was obtained as compared with a value of 304 calculated for simple acid hydrolysis of the lactam to yield an amide containing two carbonyl groups.

EXAMPLE 4.—PRODUCT D

Into the same type equipment employed in Example 1 was charged 131.5 parts of dodecenyl succinic anhydride, 43.0 parts of butyrolactone and 2.0 parts of triethylamine. The charge was heated for 3 hours at 110–120° C. at which time the neutralization number was 274. Heating was continued for an hour and 38 minutes longer and since the neutralization number remained constant, heating was discontinued. The product was completely soluble at 5% concentration in petroleum ether.

EXAMPLE 5.—PRODUCT E

Into the same type equipment employed in Example 1 was charged 133 parts of dodecenyl succinic anhydride, 43 parts of butyrolactone and 9 parts of water. The charge was heated at 97–100° C. for about 13 hours at which time the neutralization number was 302 and the product completely soluble in petroleum ether at 5% concentration.

The application of the products of the present invention as rust inhibitors was determined by a series of tests. The various products were tested to determine their solubility in petroleum oil by adding 1% by weight of the reaction product to 100 parts by weight of petroleum ether and stirring. If any residue be observed, the product is indicated as insoluble. The rust preventive properties of the chemical products were observed by carefully cleaning and polishing, in the well recognized manner for performing this test, strips of steel 3½" x ⅝" x 1/16" having an S.A.E. grade designation of 1020 and vigorously shaking each specimen in 75 cc. of petroleum ether containing the desired concentration or concentrations (from 5 to 20 parts per million of solvent) of the rust inhibitor. After standing for one-half hour, 2 cc. of distilled water were added and the sample reshaken. The strip was allowed to stand in the wet petroleum ether at room temperature for about 3 hours

nd was then removed and visually inspected for rust. he results of the tests with typical members of the new lass of reaction products are set forth in the following able:

Table I

Product	Solubility in Petroleum Ether	Steel Strip Rust Test		
		20 p.p.m.	10 p.p.m.	5 p.p.m.
	complete	none		slight.
	do	do		none.
	do	do	none	trace.
	do	do		rust.
	do	do	none	none.

Various other tests utilized in the art were also em-loyed in the further testing of chemical products of he present invention. A description of such tests and he results obtained therefrom follow.

Water tolerance test, A.S.T.M. 1094–53.—This test is ised to evaluate the emulsion characteristics of the rust nhibited petroleum fraction, such as a petroleum fuel. The apparatus consists of a 100 cc. glass stoppered grad-ated cylinder, which after thorough cleaning is rinsed horoughly with distilled water and stored completely full f distilled water until used in a test. The water is re-noved and 80 cc. of iso-octane containing 20 parts per nillion of the inhibitor under test is placed in the gradu-te and 20 cc. of distilled water added thereto and the nixture is shaken vigorously at room temperature for 2 ninutes. The mixture is then allowed to stand on a ibration-free surface for 5 minutes whereupon the vol-me of the aqueous layer and the amount of emulsion, if ny, are recorded. In order to pass the test, the fuel shall eparate sharply from the water and there shall be no vidence of an emulsion, precipitate or suspended mat-er within or upon either layer. Neither layer shall have hanged more than 1 cc. in volume.

Sea water reaction test.—This test is designed to de-ermine the solubility of the alkaline earth salts of rust nhibitors. Synthetic sea water was prepared according o the method set forth in Procedure B, A.S.T.M. D 665–53T. The method consists in adding 250 cc. of n-hep-ane containing about 200 p.p.m. of the material to be ested and 25 cc. of synthetic sea water to a 500 cc. 3-neck flask equipped with stirrer and reflux condenser and stirring for 30 minutes at room temperature. Agitation was stopped and when motion had ceased the interface was examined for scum and the walls of the flask exam-ined for precipitate of which there shall be none.

Lead salt test.—This test is designed to indicate the possibility of precipitate from the use of rust inhibitor in a leaded gasoline. In this test, an ionizable lead salt is added to assure a concentration of lead ion. The test solution is prepared by dissolving 25 parts of lead naph-thenate in 2500 parts of a regular gasoline and the solu-tion is filtered through a double thickness of filter paper and then through a layer of fuller's earth. Thereupon 100 cc. of the test solution is added to a 500 cc. 3-neck flask equipped with a stirrer and air condenser. Agita-tion is started and the rust inhibitor under test is added dropwise until about 0.5 gram has been added where-upon agitation is continued for an hour at room tempera-ture and the mixture is examined for haziness or insolu-bles with the aid of a flashlight. To pass the test there shall be no more haze than is exhibited by use of a blank test with no inhibitor present.

The rust preventing characteristics of a steam turbine oil containing a product of the present invention in the presence of water was determined by following A.S.T.M. Test D 665–53T, Procedure B thereof. The oil employed was a base stock in commercial use for the formulating of steam turbine finished lubricants and, of course, con-tained no inhibitor of any kind. In this test and the other tests described above, various reaction products of an

alkenyl succinic anhydride yielded the results shown be-low in Table II.

Table II

Product	Solubility in Petro-leum Ether	Rust Test	Sea Water Test (insol-ubles)	Water Toler-ance Test	Lead Salt Test (insol-ubles)
A	complete	pass at 20 p.p.m.	trace	pass	none.
B	do	do	none	do	Do.
C	do	do	fail	do	Do.
D	do	do		do	Do.
E	do	do	fail	do	Do.

The results of the several tests clearly show that the new reaction products of the class described are oil solu-ble, are effective in protecting ferrous iron and steel against rusting in oil-water contact and do not form con-tinuous oil-water emulsions.

It is intended to cover all changes and modifications of the examples of the invention chosen for purposes of disclosure which do not constitute departures from the spirit and scope of the invention.

This application is a division of Serial No. 678,432, filed August 15, 1957.

What is claimed is:

1. A rust preventive composition comprising a major proportion of a liquid petroleum hydrocarbon carrier and a minor proportion sufficient to inhibit rusting of a re-action product obtained by heating at 95–120° C. equal molar proportions of a member of the group consisting of 2-pyrrolidinone, 5-methyl-2-pyrrolidinone, N-methyl-pyrrolidinone, 2-piperidone, 3-methyl-2-piperidone, 3-ethyl-2-piperidone, 3-propyl-2-piperidone, oxindole, diox-indole and butyrolactone with a member of a group con-sisting of alkenyl succinic anhydrides and alkenyl suc-cinic acids, the alkenyl radical containing 8–15 carbon atoms.

2. A rust preventive composition comprising a major proportion of a petroleum fuel and a minor proportion sufficient to inhibit rusting of a reaction product obtained by heating at 95–120° C. equal molar proportions of a member of the group consisting of 2-pyrrolidinone, 5-methyl-2-pyrrolidinone, N-methylpyrrolidinone, 2-piperi-done, 3-methyl-2-piperidone, 3-ethyl-2-piperidone, 3-propyl-2-piperidone, oxindole, dioxindole and butyrolac-tone with a member of a group consisting of alkenyl suc-cinic anhydrides and alkenyl succinic acids, the alkenyl radical containing 8–15 carbon atoms.

3. A rust preventive composition comprising a major proportion of a mineral oil lubricating fraction and a minor proportion sufficient to inhibit rusting of a reac-tion product obtained by heating at 95–120° C. equal molar proportions of a member of the group consisting of 2-pyrrolidinone, 5-methyl-2-pyrrolidinone, N-methylpyr-rolidinone, 2-piperidone, 3-methyl-2-piperidone, 3-ethyl-2-piperidone, 3-propyl-2-piperidone, oxindole, dioxindole and butyrolactone with a member of a group consisting of alkenyl succinic anhydrides and alkenyl succinic acids, the alkenyl radical containing 8–15 carbon atoms.

4. A rust preventive composition comprising a major proportion of a liquid petroleum hydrocarbon carrier hav-ing dissolved therein a minor proportion sufficient to in-hibit rusting of a reaction product obtained by heating at 95–120° C. equal molar proportions of N-methyl 2-pyrrolidinone and branched chain dodecenyl succinic acid.

5. A rust preventive composition comprising a major proportion of a liquid petroleum hydrocarbon carrier having dissolved therein a minor proportion sufficient to inhibit rusting of a reaction product obtained by heating at 95–120° C. equal molar proportions of 2-pyrrolidi-none and branched chain dodecenyl succinic anhydride.

6. A rust preventive composition comprising a major proportion of a liquid petroleum hydrocarbon carrier having dissolved therein a minor proportion sufficient to

inhibit rusting of a reaction product obtained by heating at 95–120° C. equal molar proportions of 2-pyrrolidinone and branched chain dodecenyl succinic acid.

7. A rust preventive composition comprising a major proportion of a liquid petroleum hydrocarbon carrier having dissolved therein a minor proportion sufficient to inhibit rusting of a reaction product obtained by heating at 95–120° C. equal molar proportions of butyrolactone and branched chain dodecenyl succinic acid.

8. A rust preventive composition comprising a major proportion of a liquid petroleum hydrocarbon carrier having dissolved therein a minor proportion sufficient to inhibit rusting of a reaction product obtained by heating at 95–120° C. equal molar proportions of butyrolactone and branched chain dodecenyl succinic anhydride.

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