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LUBRICANTS CONTAINING AMINE SALTS OF N-SUBSTITUTED PYRROLIDONE CARBOXYLIC ACIDS

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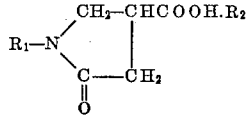
The present invention relates to corrosion inhibition and it particularly relates to corrosion inhibition using pyrrolidone carboxylic amine salts containing long chain fatty groups.

The primary object of the present invention is to provide a novel system for corrosion inhibition which involves utilizing long fatty chain substituted pyrrolidone carboxylic acid amine salts which particularly adapt themselves as petroleum additives.

A further object is to provide novel amino fatty pyrrolidone carboxylic acid amine salts which are unusually effective as corrosion inhibitors.

These substituted pyrrolidone carboxylic acid amine salts may be characterized by the following formula:



Where R_1 represents a high molecular weight group containing from 10 to 30 carbon atoms derived from a high molecular weight primary amine containing amido and amino groups in the long chain; R_2 represents a high molecular weight amine or polyamine containing 10 to 60 carbon atoms. The amine groups in the salt forming molecule may be primary, secondary or tertiary and may be part of an aliphatic structure.

These compounds have outstanding corrosion inhibiting properties in neutral, basic and acidic oils, lube oils, greases, etc. Where R_1 is derived from octadecylamine there will not be an amine group at the end of the long chain R_1 group.

Essentially the R_2 group is a primary long chain water insoluble aliphatic amine or an aryl alkyl water insoluble amine or a heterocyclic group containing two or three nitrogens having a long aliphatic side chain, said amines and aliphatic side chain containing 10 to 30 carbon atoms.

Thus the R_1 group may be the radical obtained from such high molecular weight primary amines as follows:

Octadecyl amine
Primary tallow amine
Tertiary-alkyl primary amines
Rosin primary amines
Dodecylbenzyl amine
1-aminoethyl,2-heptadecyl imidazoline
Octadecylaminopropyl amine

It will be noted that of the above amines all are primary amines with an amine group at the end of the chain and that the sixth amine terminates in a heterocyclic group and that the last amine has an amino group in the chain as well as a group at the end of the chain. All of these amines are water insoluble.

The nitrogen compound which forms the amine salt with the substituted pyrrolidone carboxylic acid should be

a high molecular weight water insoluble amine capable of forming an oil soluble salt of the substituted pyrrolidone carboxylic acid.

The following are illustrative amines:

Hexadecyl amine
Tallow amine
Di-hexadecyl amine
Dimethyl octadecyl amine
Dodecyl benzyl amine
Rosin amine
1-hydroxyethyl,2-heptadecenyl imidazoline
Octadecylaminopropyl amine (Duomeen T)
t-Octadecylamine (Primene JM–T)
Oleylaminoethyl piperazine
Tallow oxazolines (Alkaterge)

the amine forming the salt as set forth in the table above contains amino or amido groups or heterocyclic nitrogen containing rings. The above amines contain 1 to 3 nitrogen atoms. The first three primary amines are preferred in the first group set forth above and the first, second, and fourth amines are preferred in the second group above.

The substituted pyrrolidone carboxylic acids may be synthesized by reacting high molecular weight water insoluble primary amines with itaconic acid, its esters or half-esters.

Under proper conditions and if necessary, in the presence of certain catalysts, this reaction can be made almost quantitive by reacting one mol of a high molecular weight primary amine with one mol of itaconic acid to form the substituted pyrrolidone carboxylic acid, at temperatures ranging from 120° C. to 200° C.

This compound is then neutralized with one mol of amine to form the amine salt, which is readily soluble in most petroleum solvents and hydrocarbons.

The following examples are given by way of illustration and are not to be considered as limiting the invention in any way.

Example 1

Equimolar portions of itaconic acid and N-octadecylamine were mixed at 75° C. in a one liter three neck flask equipped with a Stark-Dean trap, condenser, stirrer and thermometer.

Heat was applied and the temperature slowly raised to 200° C. in two hours, during which time one mol of water was recovered in the moisture trap.

Upon cooling the product set to a hard wax-like solid containing 90% 1-octadecyl,2-pyrrolidone 4-carboxylic acid.

It was soluble in hot isopropyl alcohol and xylene, and insoluble in petroleum ether. The above compound was then melted and neutralized with one mol of tallow aminopropylamine to form an amine salt which was soluble in all proportions in gasoline, kerosene, lubricating oils and petroleum waxes.

Example 2

Equimolar portions of itaconic acid and t-octadecylamine, known as Primene JM–T (Rohm & Haas) were reacted as noted in Example 1 to yield the t-octadecyl pyrrolidone carboxylic acid.

This product was neutralized with one mol of 1-hydroxyethyl,2-heptadecenyl imidazoline to form an oil soluble compound which was found to have exceptional corrosion inhibiting properties.

Example 3

Equimolar portions of dodecylbenzyldiethylenetriamine and dibutyl itaconate was reacted as described in Example 1 and one mol of butyl alcohol was recovered in the Stark-Dean trap.

The resulting butyl ester of the carboxylic acid was hydrolized to form the carboxylic acid. This compound was then neutralized with one mol of dimethyloctadecylamine to form an oil soluble product which had good corrosion inhibiting properties.

The above substituted pyrrolidone carboxylic acid amine salts were evaluated for their corrosion inhibiting properties as outlined in U.S. Government military specification MIL–L–21260 "Lubricating Oil, Internal-Combustion Engine, Preservative." This specification covers preservative engine lubricating oil for use as a lubricant in spark-ignition and compression ignition types of reciprocating internal-combustion engines. The oil used in the test was a light viscosity oil meeting the specifications of Grade 1 in MIL–L–21260 specifications.

Viscosity at 210° F.:

Kinematic, centistokes	5.44 to 7.29
Saybolt Universal, seconds	44 to 50
Pour point, ° F. max.	−20
Flash point, ° F. min.	360

The following table shows the results obtained by immersing the steel test panels for one minute in the oil under test and properly drained for 20 hours followed by immersion for 20 hours in 500 ml. beakers containing synthetic sea water to a depth of ⅜ to ⅝ inch above the panels.

The beaker was covered with a watch glass and the temperature of the salt water during the immersion was held at 77° F. After immersion the panels were rinsed with distilled water, acetone and ASTM naphtha in rapid sequence in the order noted and then examined for corrosion and rust spots.

TABLE 1

Additive	Parts per million additive						
	50	100	200	300	400	500	1,000
None	F	F	F	F	F	F	F
Example #1	F	F	G	G	E	E	E
Example #2	F	F	G	E	E	E	E
Example #3	F	F	G	G	G	E	E

F—failed—corrosion and deep etching.
G—slight corrosion—edges badly rusted.
E—excellent—no etching, no rust spots, no corrosion.

The amount of 200 to 1000 parts per million is equivalent to .02 to 0.1%.

The critical concentrations are between 200 and 1000 parts per million in which the compounds of Examples 1, 2 and 3 vary from good to excellent.

This property can not be predicted from the properties of the individual components of the final compounds of Examples 1, 2 and 3 which have very little, if any, corrosive inhibition properties.

These small proportions of 200 to 1000 parts per million are surprisingly effective as compared to the normal proportions of 1–4% which is used with corrosion inhibitors of the nature of fatty esters, for example sorbitan dioleate.

The unusual property which results from these compounds and their high corrosion inhibition qualities appears to result from the interaction of the five-membered nitrogen ring in combination with the long chain amines with the carbon member of the ring adjacent the nitrogen of the ring being doubly bonded to oxygen.

It is found necessary to have a carboxylic acid group between the two CH_2 groups in the ring to achieve maximum corrosion inhibition with the carboxylic acid being converted into a long chain fatty amine salt.

The composition of the present application is desirably added to lubricating oils although it may also be used with other hydrocarbon fractions such as gasoline, kerosene, greases and desirably in general in an oleaginous environment.

An essential feature of the present invention resides in the fact that polyamines are utilized in the side chains attached to the basic five-membered nitrogen containing heterocyclic ring.

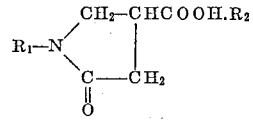
Surprisingly, the carboxylic acid by itself without the amine salt-forming group attached thereto is much less effective than the pyrrolidone carboxylic acid.

Having now particularly described and ascertained the nature of the invention, and in what manner the same is to be performed,

What is claimed is:

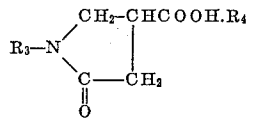
1. A petroleum oil composition consisting essentially of a major proportion of a lubricant petroleum oil and containing a pyrrolidone carboxylic acid amine salt as a corrosion inhibitor in quantities from 200 p.p.m. to 1,000 p.p.m., said amine of said amine salt being a high molecular weight primary amine containing 10 to 60 carbon atoms, water-insoluble and capable of forming an oil soluble salt of said acid and being selected from the group consisting of aliphatic amines, alkyl substituted aralkyl amines and hydroxyalkyl substituted alkylimidazolines and the pyrollidine ring of said acid having attached to the nitrogen of the ring a high molecular weight group containing from 10 to 30 carbon atoms and being selected from the group consisting of aliphatic radicals, alkyl substituted aralkyl radicals, and alkyl substituted imidazoline radicals.

2. A petroleum oil composition consisting essentially of a major proportion of a hydrocarbon petroleum lubricating oil and .02 to 0.1% of a pyrrolidone carboxylic acid amine salt of the general formula:



where R_1 is a long chain hydrocarbon containing 10 to 30 carbon atoms and R_2 is a water insoluble aliphatic amine containing 10 to 60 carbon atoms.

3. A petroleum oil composition consisting essentially of a major proportion of petroleum oil and 200 p.p.m. to 1,000 p.p.m. of a pyrrolidone carboxylic acid amine salt as a corrosion inhibitor having the general formula:



where R_3 is a high molecular weight group containing from 10 to 30 carbon atoms and being selected from the group consisting of aliphatic radicals, alkyl substituted aralkyl radicals, and alkyl substituted imidazoline radicals, and R_4 is a high molecular weight primary amine containing 10 to 60 carbon atoms which is water-soluble and capable of forming an oil soluble salt of said acid and being selected from the group consisting of aliphatic amines, alkyl substituted aralkyl amines and hydroxyalkyl substituted alkylimidazolines.

4. A petroleum oil composition consisting essentially of a major proportion of petroleum oil and .02% to 0.1% of an oil soluble pyrrolidone carboxylic acid salt of a water insoluble aliphatic amine, said pyrrolidone having attached to the nitrogen of the ring a high molecular weight group containing 10 to 30 carbon atoms and being selected from the group consisting of aliphatic radicals, alkyl substituted aralkyl radicals, and alkyl substituted imidazoline radicals and said aliphatic amine containing 10 to 60 carbon atoms.

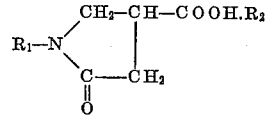
5. The composition of claim 4, said high molecular

weight group being octadecyl and said amine being tallow aminopropylamine.

6. The composition of claim 4, said high molecular weight group being tertiary octadecyl and said amine being 1-hydroxyethyl, 2-heptadecenyl imidazoline.

7. The composition of claim 4, said high molecular weight group being dodecylbenzyl and said amine being dimethyl octadecyl amine.

8. A petroleum oil composition consisting essentially of a major amount of petroleum oil and as a corrosion inhibitor from .02% to 0.1% of a pyrrolidone, high molecular weight aliphatic amine carboxylate of the formula



wherein R_2 is a high molecular weight aliphatic primary amine containing 10 to 60 carbon atoms, and R_1 is an aliphatic radical containing 10 to 30 carbon atoms.

9. A petroleum oil composition consisting essentially of a major amount of petroleum oil and from .02% to 0.1% of oil soluble high molecular weight N-alkyl, 2-pyrrolidone, 4-carboxylic acid salt of a high molecular weight alkyl amine, said alkyl amine containing 10 to 60 carbon atoms and being water insoluble, the alkyl radical of said acid having from 10 to 30 carbon atoms.

10. A petroleum oil composition consisting essentially of a major amount of petroleum oil and from .02% to 0.1% of an N-alkyl amino propyl pyrrolidone carboxylic acid salt of a water insoluble aliphatic amine containing 10 to 60 carbon atoms.

References Cited by the Examiner

UNITED STATES PATENTS

2,363,778	11/1944	Pedersen	44—63
2,757,125	7/1956	Mudrak	260—326.3 X
2,890,979	6/1959	Korner	260—326.3 X
2,908,711	10/1959	Halter et al.	252—392
2,945,863	7/1960	Buc et al.	252—392 X

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