

PATENT SPECIFICATION

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(54) LACTONE OXAZOLINES USEFUL AS OLEAGINOUS ADDITIVES

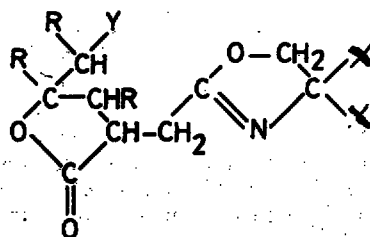
(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns alkyl lactone oxazolines, their method of preparation and the use of said lactone oxazolines in hydrocarbon fuel and lubricating compositions as highly stable anti-rust agents and/or sludge dispersants.

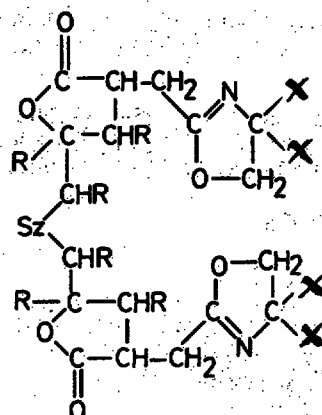
It is known that oil-soluble additives can be formed from hydrocarbyl-substituted dicarboxylic acid material which has been converted into a lactone and reacted with various amino or hydroxy compounds either through an amide, imide or ester linkage, and that these additives are useful for various functions, such as anti-rust agents, detergents or dispersants for oleaginous compositions including lube oil, gasoline, turbine oils and oils for drilling applications.

It has now been discovered that long-chain hydrocarbon structures which feature vicinal lactone and oxazoline ring systems can be obtained using novel synthetic methods whereby a highly stable additive of enhanced dispersancy, enhanced viscosity properties, and/or anti-rust properties is obtained.

The formation of the lactone oxazoline reaction product in a very high yield is effected by heating together a substantially equimolar mixture of a 2,2-disubstituted-2-amino-1-alkanol having 1 to 3 hydroxyl groups per molecule and containing a total of 4 to 8 carbon atoms per molecule and a hydrocarbon substituted lactone carboxylic acid material, the mixture being heated at 100—240°C, preferably 170—220°C until reaction is complete by infra-red analysis of the product showing maximal absorption for oxazoline. This novel class of reaction product can be represented by the formula:



wherein R is hydrogen or an alkyl radical containing from 1 to 400 carbon atoms, X is an alkyl or hydroxyalkyl group (and usually at least one of the X substituents and preferably both of the X substituents being a hydroxyalkyl group of the structure $-(CH_2)_nOH$ where n is 1 to 3) and Y is hydrogen, hydroxyl, sulfonic acid, alkylthio (TS-), alkylidithio (TSS-), or a sulfur bridge, e.g., $-S-$ and $-S-S-$, joining two lactone oxazoline units together as depicted below wherein z is a number ranging from 1 to 4 and T is defined hereafter as containing 1 to 50, preferably 2 to 20 carbons.

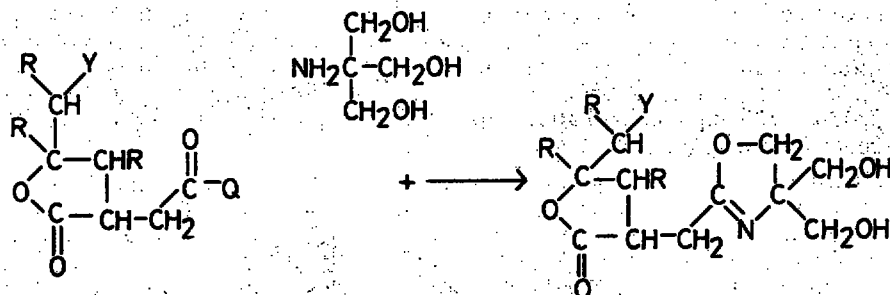


Preferred herein is polyisobutyl lactone oxazoline of number average molecular weight ranging from 400 to 100,000 prepared by the reaction of equimolar proportions of polyisobutyl lactone carboxylic acid with *tris*-(hydroxy-methyl) aminomethane at a temperature from about 100–240°C, preferably 150–180°C, until two moles of H_2O per mole of reactant are removed from the reaction.

Hydrocarbon-substituted lactone carboxylic acids, esters or amides can be obtained by the process described in our copending application 7943184 (Serial No. 1592671), which involves oxidation or thiolation of a mono unsaturated hydrocarbyl substituted C_4 to C_{10} dicarboxylic acid ester or anhydride.

The compounds which are hydrocarbon-soluble are those compounds having at least a total of 8 carbon atoms in the substantially saturated aliphatic hydrocarbyl groups and a carboxylic acid group of the dicarboxylic acid material converted into a lactone ring and another carboxylic acid group converted into an oxazoline ring as a result of the reaction of substantially equimolar amounts of said hydrocarbon substituted dicarboxylic acid lactone material and a 2,2-disubstituted - 2 - amino - 1 - alkanol having 1 to 3 hydroxy groups and containing a total of 4 to 8 carbon atoms per molecule.

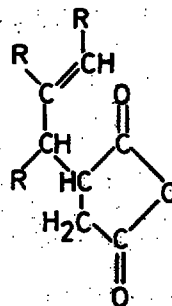
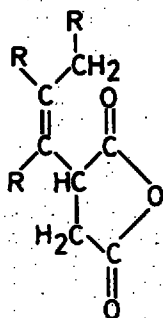
These novel alkyl lactone oxazolines of the present invention can be prepared by heating together a substantially equimolar mixture of an alkyl lactone carboxylic acid, ester or amide with a C_4 to C_8 2,2-disubstituted - 2 - amino - 1 - alkanol having 1 to 3 hydroxy groups per molecule, such as *tris* - (hydroxymethyl) aminomethane, as expressed in the following equation:



where $Q=OH$, OR or NHR .

The preparation of the required reactants involves a lactonization of an alkenyl succinic acid analog obtained via the 'Ene' reaction of an olefin with an alpha-beta unsaturated C_4 to C_{10} dicarboxylic acid, anhydride or ester thereof, such as fumaric acid, itaconic acid, maleic acid, maleic anhydride or dimethyl fumarate.

The dicarboxylic acid material can be illustrated by an alkenyl-substituted anhydride which may contain a single alkenyl radical or a mixture of alkenyl radicals variously bonded to the cyclic succinic anhydride group, and is understood to comprise such structures as:



wherein R may be hydrogen or hydrocarbyl or substituted hydrocarbyl each having from 1 to 400 carbon atoms, and preferably from 1 to 200 carbon atoms. The anhydrides can be obtained by well-known methods, such as the reaction between an olefin and maleic anhydride or halosuccinic anhydride or succinic ester (U.S. Pat. No. 2,568,876). In branched olefins, particularly branched polyolefins, R may be hydrogen, methyl or a long-chain hydrocarbyl group.

Suitable olefins include butene, isobutene, pentene, decene, dodecene, tetradecene, hexadecene, octadecene, eicosene, and polymers of propylene, butene, isobutene, pentene and decene and halogen-containing olefins. The olefins may also contain cycloalkyl and aromatic groups. The most preferred alkenyl succinic anhydrides are those in which the alkenyl group contains a total of from 4 to 400 carbon atoms; from 4 to 20 carbon atoms for aqueous systems; and at least 8 to 400 and more preferably 10 to 300 for hydrocarbon systems.

Preferred olefin polymers for reaction with the unsaturated dicarboxylic acids are polymers comprising a major molar amount of C₂ to C₈ monoolefin, e.g., ethylene, propylene, butylene, isobutylene and pentene. The polymers can be homopolymers, such as polyisobutylene, as well as copolymers of two or more of such olefins such as copolymers of ethylene and propylene, butylene and isobutylene or of propylene and isobutylene. Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 20 mole% is a C₄ to C₁₈ non-conjugated diolefin, e.g., a copolymer of isobutylene and butadiene or a copolymer of ethylene, propylene and 1,4-hexadiene.

The olefin polymers will usually have number average molecular weights within the range of 750 and 200,000 more usually between 1000 and 20,000. Particularly useful olefin polymers have number average molecular weights within the range of 900 and 3000 with approximately one terminal double bond per polymer chain. An especially valuable starting material for a highly potent dispersant additive is polyalkenes, e.g. polyisobutylene, having up to 10,000 carbon atoms.

Especially useful when it is desired that the dispersant additives also possess viscosity index improving properties are 5,000 to 200,000, e.g., 25,000 to 100,000 number average molecular weight polymers. An especially preferred example of such a V. I. improving polymer is a copolymer of 30 to 85 mole% ethylene, 15 to 70 mole% C₃ to C₈ mono- α -olefin, preferably propylene, and 0 to 20 mole% of a C₄ to C₁₄ non-conjugated diene.

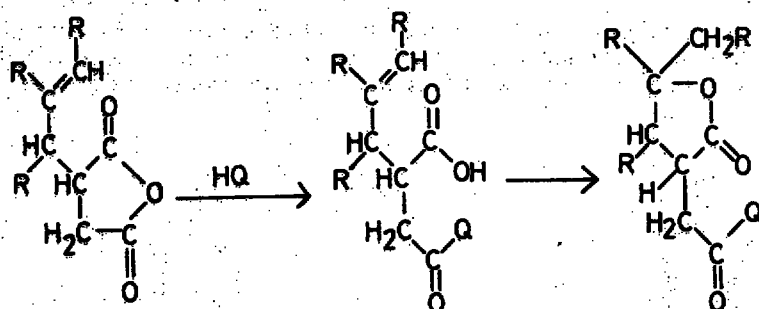
Unsubstituted or simple lactone reactants (Y=H) are readily obtained by the acid-catalyzed lactonization of an alkenyl dicarboxylic acid analog, the latter being derived from the ring scission of an alkenyl succinic anhydride with water, an alcohol or an amine as shown below wherein HQ represents water, alcohols containing from 1 to 10 carbon atoms per molecule and dialkyl amines containing from 2 to 10 carbon atoms per molecule and R is as previously defined.

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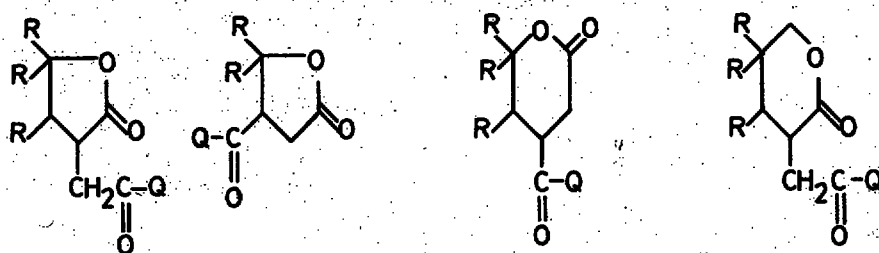
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The reaction with HQ is assumed to open the anhydride at the least congested carbonyl group and form a succinic acid, hemi-ester or amic acid product which in the presence of an acid catalyst cyclizes mostly to the 5-ring lactone product as shown above.

It is possible to use alkenyl substituents with the double bond in the 1, 2, or 3-position or even double bonds further out on the hydrocarbyl chain since the acid catalyst is capable at moving it into a position suitable for lactone formation. In general, the size of the lactone ring formed will depend upon, inter alia, the position of the double bond, and which carboxylic acid group participates in the lactone forming reaction. As a consequence, both 5- and 6-ring (or larger ring) lactones can be envisaged as illustrated below:

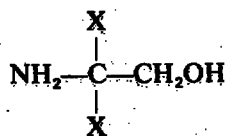


For convenience, the products of the present invention are usually shown as 5-ring lactones although larger ring lactone products can also be present.

The intramolecular cyclization step must be carried out in the presence of an acid-type catalyst in order to effect formation of the lactone. Suitable catalysts include the mineral acids such as hydrochloric acid, sulfuric acid, perchloric acid, and phosphoric acid; the sulfonic acids such as the alkanesulfonic acids and the arylsulfonic acids; the Lewis type acids such as aluminum chloride boron trifluoride, antimony trichloride, and titanium tetrachloride and low molecular weight sulfonic acid-type ion exchange resin materials, such as cross-linked sulfonated polystyrene, which is commercially available as Dowex-50. (registered Trade Mark). The alkane-sulfonic acid catalysts are preferably the lower alkanesulfonic acids containing from 1 to 12 carbon atoms per molecule, for example, methanesulfonic acid, ethanesulfonic acid, propane-sulfonic acid, and butanesulfonic acid. If desired, a mixture of lower alkanesulfonic acids can be used and such a mixture containing methane, ethane, and propanesulfonic acids is commercially available. Ordinarily, the alkanesulfonic acid will comprise from 92% to 95% sulfonic acid, from 1 to 2% sulfuric acid, and from 3 to 6% water. The arylsulfonic acid catalyst which can be used in the process includes the benzenesulfonic acids, toluenesulfonic acid, and chlorobenzenesulfonic acids, with p-toluenesulfonic acid and 4-chloro-benzenesulfonic acid being preferred. The amount of catalyst used is determined to a considerable extent by the temperature selected for conducting the reaction. Thus, at higher temperatures the amount of catalyst required in the reaction is less than when lower temperatures are used and the use of excessive amounts of catalyst at the more elevated temperatures will promote the formation of undesired side products. Ordinarily, the amount of catalyst used will be between about 0.1% up to 10% by weight of the amount of the alkenyl succinic anhydride reactant.

The presence of certain heteroatoms adjacent to the novel lactone oxazoline ring combination oftentimes endows the novel lactone oxazoline system with other desirable properties such as antioxidation and anticorrosion activity.

The amino alcohol used to react with the lactone to provide the oxazoline ring is a 2,2-disubstituted-2-amino-1-alkanol containing a total of 4 to 8 carbon atoms per molecule, and which can be represented by the formula:



wherein X is hydrogen, an alkyl, or hydroxyalkyl group, usually with at least one of the X substituents, and preferably both of the X substituents, being a hydroxyalkyl group of the structure $-(\text{CH}_2)_n\text{OH}$, wherein n is 1 to 3.

Examples of such 2,2-disubstituted amino alkanols, include 2-amino-2-methyl-1,3-propanediol, 2-amino-2-(hydroxymethyl)-1,3-propanediol (also known as *tris*-hydroxyaminomethane or THAM) and 2-amino-2-ethyl-1,3-propanediol. Because of its effectiveness, availability, and cost, THAM is particularly preferred.

By sharp contrast, we have found that other amino alcohols such as ethanolamine, propanolamine and butanolamine which lack 2,2-disubstitution, do not give oxazoline products. Similarly, the prior art (British Patent 1,420,962) clearly teaches that ethanolamine reacts with lactone acids to give amide derivatives via cleavage of the lactone ring. We have discovered that interaction of lactone acids, esters and amides with 2,2-disubstituted amino alcohols is unique, in that the lactone ring of the reactant remains intact and novel lactone oxazoline products are formed exclusively.

Inert solvents which may be used in the above reaction include hydrocarbon oils, e.g. mineral lubricating oil, kerosene, neutral mineral oils, xylene or halogenated hydrocarbons.

Although not necessary, the presence of small amounts, such as .01 to 2 wt.%, preferably 0.1 to 1 wt.%, based on the weight of the reactants, of a metal salt can be used in the reaction mixture as a catalyst.

The metal salt can be left in the reaction mixture, as it appears to become stably dispersed, or dissolved, in the reaction product, and depending on the metal, it may even contribute performance benefits to the oil or gasoline. This is believed to occur with the use of zinc catalysts in lubricants.

Metal salts that may be used as catalysts in the invention include carboxylic acid salts of Zn, Co, Mn and Fe. The carboxylic acids used to prepare the desired catalysts, include C₁ to C₁₈, e.g., C₁ to C₈ acids, such as the saturated or unsaturated mono- and dicarboxylic aliphatic hydrocarbon acids, particularly fatty acids. Specific examples of such desired carboxylic acid salts include zinc acetate, zinc formate, zinc propionate, zinc stearate, manganese(ous) acetate, iron tartrate and cobalt(ous) acetate. Completion of the oxazoline reaction can be readily ascertained by using periodic infrared spectral analysis for following oxazoline formation (C=N absorption band at 6.0 microns) until maximized relative to lactone absorption or by the cessation of water evolution.

The oil-soluble lactone oxazoline reaction products of the invention can be incorporated in a wide variety of oleaginous compositions. They can be used in lubricating oil compositions, such as automotive crankcase lubricating oils or automatic transmission fluids, in concentrations generally within the range of about 0.01 to 20 weight percent, e.g. 0.1 to 10 weight percent, preferably .3 to 3.0 weight percent, of the total composition. The lubricants to which the lactone-oxazoline products can be added include not only hydrocarbon oils derived from petroleum but also include synthetic lubricating oils such as polyethylene oils, alkyl esters of dicarboxylic acid, complex esters of dicarboxylic acids, polyglycols and alcohols, and mixtures of mineral lubricating oil and synthetic oils in any proportion.

When the products of this invention are used as multifunctional additives having detergency and anti-rust properties in petroleum fuels such as gasoline, kerosene, diesel fuels, fuel oil and other middle distillate, a concentration of the additive in the fuel in the range of 0.001 to 0.5 weight percent, based on the weight of the total composition, will usually be employed.

When used as an antifoulant in oil streams in refinery operations to prevent fouling of process equipment, such as heat exchangers, or in turbine oils, about 0.001 to 2 wt.% will generally be used.

The additive may be conveniently dispensed as a concentrate comprising 20 to

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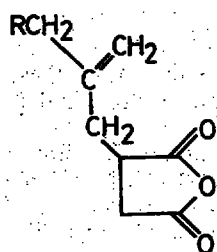
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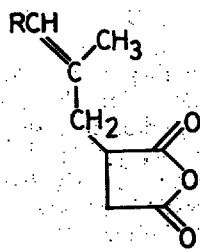
90 parts by weight of the additive dissolved in 10 to 80 parts of a mineral lubricating oil.

Preparation 1 (Dibsalac)

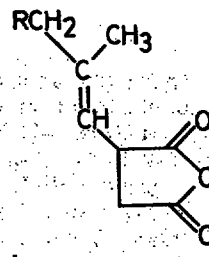
Thirty grams (0.143 mole) of diisobutenyl succinic anhydride (DIBSA), which can be a mixture of three isomers (A, B and C) depending on the mode of synthesis, were mixed.



A



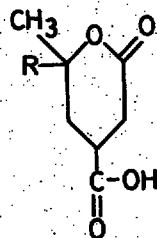
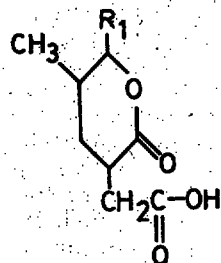
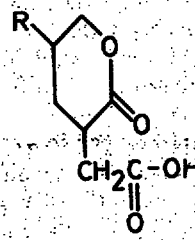
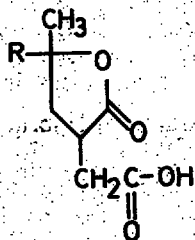
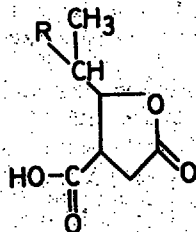
B



C

R=t-butyl

with 2.6 g of water and three drops of concentrated sulfuric acid. The mixture was heated to 110—120°C. for one hour. Infrared analysis of the reaction mixture showed that lactone formation was virtually complete. The addition of 200 ml of ether and subsequent cooling of the resulting ether solution caused solids to separate from solution. Three crops of white solid amounting to 27.1 g were collected and recrystallized from ether-acetone solution. The product, m.p. 141—142°C., featured an IR spectrum with intense carbonyl absorption bands at 5.70 (lactone) and 5.82 (carboxylic acid) microns and analyzed for 62.78% C and 9.14% H (Theory: 63.13% C and 8.86% H). The product, DIBSALAC, presumably could be one or more of the isomeric lactones depicted below. The proton and IR spectral data suggest that the 5-ring lactone acid products



R=neo-pentyl; R₁=t-butyl

predominate when reactant A is employed in the lactonization process.

Preparation 2 (Nosalac)

One mole (210 g) of n-2-octenylsuccinic anhydride (NOSA) and 1.1 mole (20 g) of water were combined and heated at 100°—110°C for about a half hour. A quantitative conversion to n-2-octenylsuccinic acid occurred. Five drops of concentrated sulfuric acid were added to the latter, and the mixture was then

heated for 16 hours at about 155°C. Upon cooling, the liquid product gradually crystallized. The white solids, m.p. 94–95°C., were isolated in high yield and featured an IR spectrum with strong absorption bands at 5.65 and 5.82 microns. The lactone acid analyzed for 63.49% C and 8.35% H, and judging from its IR spectrum (carbonyl absorption at 5.65 microns) is mainly a 5-ring lactone although some 6-ring lactone products can also form depending upon reaction conditions.

Preparation 3 (Osalac)

A half mole (175 g) of 2-octadecenyl succinic anhydride (OSA) and 0.55 mole (10 g) of water were mixed and heated in a reaction flask for a half hour at 80°C. Infrared analysis showed that complete conversion of the anhydride to succinic acid had occurred. While stirring at 80°C., 0.5 g of concentrated sulfuric acid was added, and the reaction temperature was increased to 130–140°C. Heating at 140°C. for 1.5 hours completely converted the dicarboxylic acid to the desired lactone acid products. When the cooled mixture was diluted with ether, a white solid separated from solution. Infrared analysis of the isolated solids revealed the presence of a 5-ring lactone acid (strong bands at 5.67 and 5.82 microns). Cooling the supernatant liquid gave more solids. Further fractional crystallization of later crops gave 6-ring lactone acid products. The combined weight of all crops revealed that the yield of lactone acid product was quantitative. A recrystallized sample of 5-ring lactone product melted at 112°C. and analyzed for 71.50% carbon, 10.77% H and 16.67% oxygen. Theory requires 71.49% C, 11.18% H, and 17.32% O.

Preparation 4 (Pibsalac)

One hundred twenty grams of polyisobutenyl succinic anhydride (PIBSA) of MW about 960 and have a saponification number (Sap. No.) of 92 were diluted in 100 ml of tetrahydrofuran (THF). Two grams of water were added and the resulting mixture was heated to reflux temperature for about two hours. Infrared analyses of the mixture showed that the anhydride was fully converted to the succinic acid analog. The THF solvent was boiled off and 1 ml of concentrated sulfuric acid was added to the mixture at about 110°C. Heating for two hours at 120°C. effected the conversion of the polyisobutenyl succinic acid to the desired lactone acid product. Infrared analyses showed the presence of strong absorption bands at about 6.5–8.5 microns.

The mixture was diluted in 200 ml of hexane, washed twice with 200 ml of water and subsequently concentrated by rotoevaporation for two hours at 80°C. Infrared analysis of the lactone acid product treated with diethylamine featured an intense absorption band at 5.64 microns (5-ring lactone carbonyl stretching).

Preparation 5 (Pibsalac)

A mixture of 140 g (0.1 mole) of polyisobutenyl succinic anhydride (MW about 960 and having a saponification number (Sap. No.) of 92), 3 g of water and 1 g of concentrated sulfuric acid were heated for about three hours at 105°C. Infrared analysis indicated that the anhydride was directly and completely converted to the desired lactone acid as evidenced by the strong carbonyl absorption bands at 5.63 to 5.84 microns. The reaction product was treated with 0.02 mole of NaOH (dissolved in tetrahydrofuran), filtered and rotoevaporated at 80°C. for four hours. The IR spectrum of the amber concentrate treated with an excess of diethylamine showed a strong lactone carbonyl absorption at 5.65 microns.

Preparation 6 (Nosalac Amide)

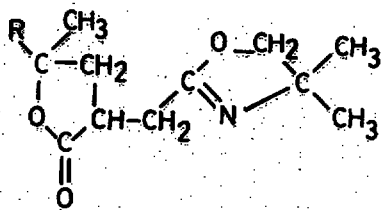
Twenty-eight grams of the lactone acid product prepared in Preparation 2 (mainly n-hexyl butyrolactone- α -acetic acid) were treated with an excess of gaseous ammonia at 180°C for about two hours. The product was dissolved in hot xylene and filtered. Upon cooling the solution, a solid product precipitated. The dried product (15 g) melted at 117–119°C., showed an IR spectrum with dominant bands at 5.65 and 6.0 microns and analyzed for 62.75% C, 9.29% H and 6.18% N. Theory for the lactone amide requires 63.40% C, 9.31% H and 6.18% N.

Preparation 7 (Hydroxy Pibsalac)

A mixture comprising 0.32 mole (410 g) of PIBSA (MW about 960) with a saponification number of 83, 0.32 mole (36.3 g) hydrogen peroxide (30% aqueous solution) and 0.4 g (0.1 wt.% of concentrated sulfuric acid) was heated with stirring at about 120°C. for approximately five hours. Infrared analysis showed the presence of carbonyl bands ascribable to lactone acid. The product was diluted with an equal volume of neutral oil.

Example 1 (Dibsalac Oxazoline)

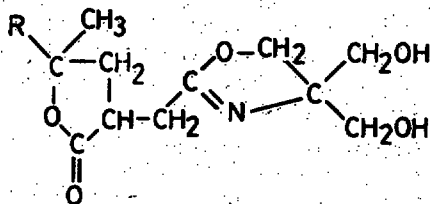
Eleven grams (0.045 mole) of Dibsalac described in Preparation 1 was dissolved in 20 ml of xylene and 4.65 g (0.048 mole) of 2-amino-2-methyl-1-propanol was added dropwise. The reaction mixture was heated to reflux in a flask equipped with a Dean-Stark moisture trap. After 16 hours, 1.5 ml of water were collected and the xylene was removed by reboevaporation. Vacuum distillation of the residue afforded a colorless liquid, b.p. 135°C. (0.3 mm) in about 85% yield. The liquid gradually crystallized on standing. The crystalline product featured an infrared spectrum with prominent lactone and oxazoline absorption bands at about 5.68 and 6.02 microns, and analyzed for 68.15% carbon, 9.48% hydrogen, 4.93% nitrogen and 16.54% oxygen. Theory for the lactone oxazoline ($C_{18}H_{27}NO_3$) requires 68.28% carbon, 9.6% hydrogen, 4.99% nitrogen and 17.06% oxygen. The proposed structure is shown below.



R=neo-pentyl

Example 2 (Dibasalac Oxazoline)

Dibasalac (0.05 mole, 11.4 g) described in Preparation 1 and 0.05 mole (6.2 g) of tris-(hydroxymethyl)-aminomethane (THAM) were added to 25 ml of xylene in a reactor equipped with a Dean-Stark moisture trap. The mixture was refluxed until ca. 1.6 ml of water were collected in the moisture trap (approximately 5 hours). Infrared analysis indicated complete conversion to lactone oxazoline product. Upon cooling to room temperature, the clear solution became cloudy and white solid separated from solution. The solid product was filtered off, washed several times with ether, and dried. The first crop weighed 6.0 grams and melted at 82–88°C. Recrystallization from xylene gave a white solid which melted at 97–103°C., and featured an IR spectrum with prominent lactone carbonyl and oxazoline (C=N) absorption bands at 5.66 and 6.0 microns. The recrystallized solid analyzed for 59.87% C, 8.46% H and 4.26% N. Theory for the lactone oxazoline hemi-hydrate ($C_{18}H_{27}NO_5 \cdot 1/2H_2O$) requires 60.15% C, 7.89% N, and 4.38% N. The product can be represented by the following structure:



R=neo-pentyl

Example 3 (Nosalac Oxazoline)

Nosalac amide (0.025 mole, 5.67 g) described in Preparation 6 and 0.025 mole (3.0 g) of THAM were added to 10 ml of xylene and the mixture was refluxed overnight. The solvent was stripped off and the mixture was heated to 200° for two hours, then cooled and dissolved in benzene. The addition of ether to the benzene solution caused the gradual precipitation of solid from solution. The IR spectrum of the solid, m.p. 108–109°C., featured characteristic lactone carbonyl and oxazoline (C=N) absorption bands at 5.63 and 6.0 microns, and analyzed for 61.57% C, 8.38% H and 4.69% N. Theory for the adduct ($C_{18}H_{27}O_5N$) requires 61.32% C, 8.69% H and 4.47% N.

Example 4 (Osalac Oxazoline)

Two tenths mole (73.6 g) of Osalac described in Preparation 3 and 0.2 mole (24.2 g) of tris-hydroxymethyl aminomethane (THAM) were added to 100 ml of xylene contained in a reactor equipped with a Dean-Stark moisture trap. The mixture was refluxed until 5 ml of water were collected (about three hours) and the xylene solvent was then removed by rotoevaporation. The product was diluted in ether and two crops amounting to 71 g were isolated by filtration. The product melted at 121–122°C., and featured an IR spectrum with prominent lactone carbonyl and oxazoline (C=N) absorption bands. Elemental analyses showed 66.86% C, 10.61% H, 3.45% N and 12.01% O. Theory for the OSALAC oxazoline ($C_{26}H_{47}NO_5$) required 66.86% C, 10.44% H, 3.09% N and 12.63% O.

Example 5 (Pibsalac Oxazoline)

Sixty grams (ca. 0.05 mole) of Pibsalac described in Preparation 4 and 6.1 g (0.05 mole) of tris-(hydroxymethyl)aminomethane (THAM) were added to 50 ml of tetrahydrofuran (THF). The stirred mixture was gradually heated to dissolve the reactants.

The THF solvent was then boiled off, and the reaction temperature was raised to 170° and kept there for about an hour. The residue was dissolved in hexane, filtered and rotoevaporated at 90°C. for four hours, and diluted with an equal weight of neutral oil. The infrared spectrum of the product featured prominent lactone carbonyl and oxazoline (C=N) absorption bands at 5.63 and 6.0 microns.

The diluted product (50% a.i.) showed a hydroxyl number of 43.1 and analyzed for 0.69% nitrogen (by Kjeldahl). The basic nitrogen content, determined by non-aqueous titration with perchloric acid was 0.56%.

Example 6 (Pibsalac Oxazoline)

The Pibsalac prepared in Preparation 5 and 0.1 mole (12.0 g) of tris-(hydroxymethyl) aminomethane (THAM) were combined and heated at 180°C for about four hours. The product was diluted in 200 ml hexane, filtered and rotoevaporated at 90°C. for four hours. The residue was diluted in an equal weight of neutral oil (S-150N). IR analysis of the product showed strong absorption bands at 5.65 and 6.0 microns ascribable to lactone and oxazoline functionality. Analyses revealed that the polyisobutyl lactone oxazoline product contained 0.63% nitrogen by Kjeldahl's method and 0.56 basic nitrogen as determined by non-aqueous titration with perchloric acid. The hydroxyl number of the diluted product (50% a.i.), as determined according to AM-S 240, 10-1, was 51.2.

Example 7 (Hydroxy-pibsalac Oxazoline)

The hydroxy PIBSA lactone acid (ca. 0.05 mole, 130 g of 50% a.i.) described in Preparation 7 and 0.05 mole (6.05 g) of THAM were mixed and heated to 180°C. for about four hours. The product was diluted in 100 ml hexane, filtered and concentrated by rotoevaporation. The diluted product (50% a.i.) featured an IR spectrum with lactone carbonyl and oxazoline (C=N) absorption bands at 5.7 and 6.03 microns.

Comparative Test 1**Chemical Stability of Pibsalac Oxazoline**

Fifteen grams of the product of Example 5 and 1 gram of THAM were combined and heated at 195°C. for six hours. The infrared spectrum of the reaction mixture was virtually identical to that of the Pibsalac Oxazoline reactant indicating that the lactone oxazoline was resistant to further aminolysis by THAM. By way of contrast, treatment of polybutenyl succinic anhydride/mono-THAM ester (formed by reacting polybutenyl succinic anhydride with one mole of THAM at 170° for several hours) with THAM under similar conditions converted the mono-oxazoline ester completely to the bisoxazoline product in less than an hour.

Comparative Test 2**Thermal Stability of Pibsalac Oxazoline**

Heating the product of Example 5 at 200°C. for about 20 hours caused no observable changes in its infrared spectrum. Under similar thermolysis conditions, polybutenyl-bis-oxazoline (prepared from polybutenyl succinic anhydride and 2 moles of THAM at 180° for 2 hours) showed distinct changes in its infrared spectrum. Heating caused the dominant absorption band at 6.0 microns (C=N stretching) (characteristic of oxazolines) to gradually diminish and become less intense than the imide-type absorption band (at about 5.85 microns) which eventually dominated the spectrum of the thermalized material after 20 hours.

Example 8

Sludge Inhibition Bench (SIB) Test

The product of Example 5 and two other dispersant additives were subjected to a Sludge Inhibition Bench (SIB) Test which has been found after a large number of evaluations, to be an excellent test for assessing the dispersing power of lubricating oil dispersant additives.

The medium chosen for the Sludge Inhibition Bench Test was a used crankcase mineral lubricating oil composition having an original viscosity of about 325 SUS at 100°F. that had been used in a taxicab that was driven generally for short trips only, thereby causing a buildup of a high concentration of sludge precursors. The oil that was used contained only a refined base mineral lubricating oil, a viscosity index improver, a pour point depressant and zinc dialkyldithiophosphate antiwear additive. The oil contained no sludge dispersants. A quantity of such used oil was acquired by draining and refilling the taxicab crankcase at 1000-2000 mile intervals.

The Sludge Inhibition Bench Test is conducted in the following manner. The aforesaid used crankcase oil, which is milky brown in color, is freed of sludge by centrifuging for 1/2 hour at about 39,000 gravities (gs.). The resulting clear bright red supernatant oil is then decanted from the insoluble sludge particles thereby separated out. However, the supernatant oil still contains oil-soluble sludge precursors which on heating under the conditions employed by this test will tend to form additional oil-in-soluble deposits of sludge. The sludge inhibiting properties of the additives being tested are determined by adding to portions of the supernatant used oil, a small amount, such as 0.5, 1.0 or 1.5 weight percent, on an active ingredient basis, of the particular additive being tested. Ten grams of each blend being tested is placed in a stainless steel centrifuge tube and is heated at 280°F. for 16 hours in the presence of air. Following the heating, the tube containing the oil being tested is cooled and then centrifuged for 30 minutes at about 39,000 gs. Any deposits of new sludge that form in this step are separated from the oil by decanting the supernatant oil and then carefully washing the sludge deposits with 15 ml. of pentane to remove all remaining oil from the sludge. Then the weight of the new solid sludge that has been formed in the test, in milligrams, is determined by drying the residue and weighing it. The results are reported as milligrams of sludge per 10 grams of oil, thus measuring differences as small as 1 part per 10,000. The less new sludge formed the more effective is the additive as a sludge dispersant. In other words, if the additive is effective, it will hold at least a portion of the new sludge that forms on heating and oxidation, stably suspended in the oil so it does not precipitated down during the centrifuging.

Using the above described test, the dispersant action of the lactone-oxazoline additives of the present invention was compared with the dispersing power of a commercial dispersant referred to as PIBSA/TEPA. The PIBSA/TEPA was prepared by reaction of 1 mole of tetraethylene pentamine with 1.5 moles of polyisobutenyl succinic anhydride (Sap. No. 80) obtained from polyisobutylene of about 1000 number average molecular weight. The PIBSA/TEPA dispersant was used in the form of an additive concentrate containing about 50 weight percent PIBSA/TEPA in 50 wt.% mineral lubricating oil. This PIBSA/TEPA additive concentrate analyzed about 1.8% nitrogen, indicating that the active ingredient, i.e., PIBSA/TEPA per se, contained about 3.6% nitrogen.

In addition, the lactone-oxazoline product of the present invention was also compared with polyisobutenylsuccinic anhydride-bis-oxazoline material prepared in accordance with the teachings of German Serial DOS 2512201 in the Sludge Inhibition Bench Test. The bis-oxazoline designated PIBSA/Bis-THAM dispersant was prepared via the reaction of 2 molar proportions of tris-(hydroxymethyl) aminomethane with polyisobutenylsuccinic anhydride according to the procedure, stoichiometry and reaction conditions specified in the above patent application. The test results are given in the table below.

TABLE
Sludge Dispersancy Test Results

Additive	Milligrams Sludge/10 g. Oil at			
	%N	0.5 wt.%	1.00 wt%	1.5 wt%
of Example 5	0.69	7.70	4.37	0.0
Blank		10.0	10.0	10.0
PIBSA/BisTHAM	1.0	7.61	4.17	0.56
PIBSA/TEPA	1.2	7.78	3.44	2.22

The data of this Table illustrates the outstanding dispersant activity of the additive products of the invention when compared with a known commercial dispersant referred to as PIBSA-TEPA.

The oxidation resistance is illustrated by a test in which air is bubbled through lubricant samples maintained at about 160°C. over a 48-hour period. Each 300 gram sample is modified by the addition of about 5.5 volume percent (50% a.i.) dispersant to measure its respective effect in reducing thickening. Twenty parts per million of iron acetylacetonate is added to each sample at the beginning and again at the end of 24 hours. At the end of the test the result were as follows:

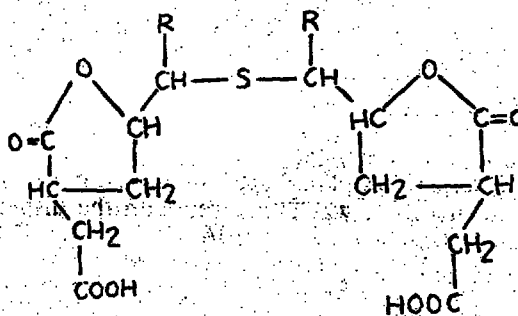
Example	Dispersant Added	Viscosity Poises @ -18°C
1	none	46
2	Example 5 additive	68
3	PIBSA-TEPA	80

Example 9

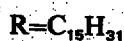
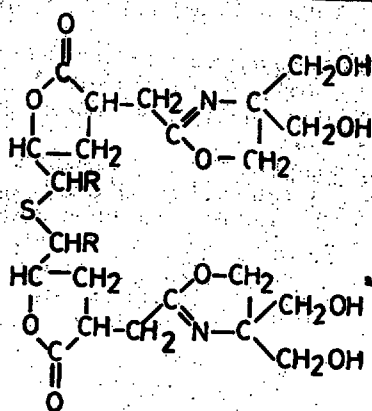
(Thio-bis-osalac Oxazoline)

Two-tenths mole (73.6 g) of octadecenyl succinic acid was dissolved in 500 ml ether and a tenth mole (10.3 g) of SCl_2 was added dropwise to the stirred ether solution at about 25°C. The addition was exothermic (ether refluxed) and HCl evolution occurred. The mixture was refluxed for about 8 hours. Upon cooling solids separated from solution. The solid product featured an infrared spectrum with prominent lactone and carboxylic acid carbonyl absorptions at 5.62 and 5.82 microns, melted at 158–163°, and analyzed for 69.01% C, 10.17% H, 4.37% S and 16.74% O. Theory for the lactone acid ($\text{C}_{44}\text{H}_{78}\text{O}_6\text{S}$) requires 68.88% C, 10.25% H, 4.18% S and 16.69% O.

Further refluxing the supernatant liquid gave four more crops of product with a combined weight of 50 g. The yields were quantitative. The proposed structure for thio-bis-Osalac is illustrated below:



Thio-bis-Osalac (0.05 mole, 38.4 g) as prepared above and THAM (0.1 mole, 12.1 g) were added to xylene (200 ml) in a reactor fitted with a moisture trap. The mixture was refluxed until about 3 ml of water were collected in the moisture trap (three hours). The hazy xylene solution was filtered, and diluted with acetone to the cloud point. The solids that separated from solution were recovered by filtration. Four crops amounting to 47.5 g were collected. The solid product, m.p. 171–175°C featured an IR spectrum with prominent absorption bands at 5.63 and 6.0 microns, and analyzed for 64.95% C, 9.07% H, 3.03% N and 2.92% S. Theory for the thio-bis-lactone oxazoline ($\text{C}_{52}\text{H}_{92}\text{N}_2\text{O}_{10}\text{S}$) requires 66.63% C, 9.89% H, 3.00% N and 3.42% S. A plausible structure is shown below:



Example 10

(Thio-bis-Pibsalac Oxazoline)

Approximately 130 g of polyisobutenylsuccinic acid (MW about 960) (prepared via hydrolysis of PIBSA having a saponification number of about 84) were dissolved in 400 ml of chloroform and 0.05 mole (5.3 g) of SCl_2 was added dropwise to the stirred solution. After refluxing the mixture overnight, two drops of sulfuric acid were added, the solvent was stripped off, and the mixture heated at about $100^\circ C$ overnight. The product (Thio-bis-Pibsalac) featured an infrared spectrum with strong absorption bands in the 5.6—5.8 micron region and analyzed for 1.69% sulfur and 0.09% chlorine. The IR spectrum of the diethylamine-treated product revealed a strong lactone carbonyl band at 5.63 microns.

Thio-bis-Pibsalac (0.01 mole, 26.3 g) as prepared above, THAM (0.02 mole, 2.42), and 0.01 g of zinc acetate were added to 26 g of neutral oil (S-150N) and heated to $180^\circ C$ for about two hours. The IR spectrum of the product showed absorption bands at 5.65 (lactone) and 6.0 (oxazoline) microns. The diluted product (50% a.i.) analyzed for 0.54% N.

Example 11

Sulfur Pibsalac Oxazoline

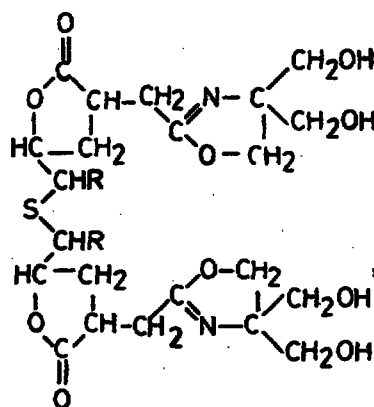
Seventy grams (0.05 mole) of PIBSA (MW about 960 with A Sap. No. of about 83) were dissolved in 100 ml of tetrahydrofuran (THF) and 6 g (0.05 g) of chlorosulfonic acid were added dropwise to the stirred THF solution at about $25^\circ C$. The addition was exothermic and external cooling was necessary to maintain the reaction temperature at about $25^\circ C$. After addition the reaction mixture was stirred at room temperature for an hour, and then 1.0 g of water was added and the mixture was heated at reflux for 2 hours. The THF was stripped off and the residue dissolved in 200 ml of hexane. The hexane solution was washed twice with 100 ml of water, dried, and rotoevaporated at $80^\circ C$ for 4 hours. The concentrate featured an IR spectrum with strong lactone absorption bands at 5.6—5.71 microns indicating a mixture of 5- and 6-ring lactones, and analyzed for 1.92% sulfur.

Twenty-six grams of the sulfo Pibsalac were dissolved in 26 g of neutral oil, and combined with 5 grams of THAM, and 0.01 g of $ZnAc_2$. The mixture was heated to $180^\circ C$ for about 4 hours, diluted in hexane, filtered and rotoevaporated at $80^\circ C$ for 2 hours. Infrared analysis of the product showed the presence of lactone and oxazoline functionality.

WHAT WE CLAIM IS:—

1. A lactone oxazoline reaction product when obtained by heating together at a temperature in the range of 100 — $240^\circ C$ a substantially equimolar mixture of a hydrocarbon-substituted lactone carboxylic acid material and a 2,2-disubstituted-2-amino-1-alkanol having 1 to 3 hydroxy groups per molecule and containing a total of 4 to 8 carbon atoms per molecule, the reaction mixture being heated for such period of time until infrared absorption for oxazoline is maximal indicating completion of the oxazoline reaction.

2. A reaction product according to claim 1 wherein said acid material is an acid, amide or ester and said amino-alkanol has the formula



Example 10

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Thio-bis-Pibsalac (0.01 mole, 26.3 g) as prepared above, THAM (0.02 mole, 2.42), and 0.01 g of zinc acetate were added to 26 g of neutral oil (S-150N) and heated to $180^\circ C$ for about two hours. The IR spectrum of the product showed absorption bands at 5.65 (lactone) and 6.0 (oxazoline) microns. The diluted product (50% a.i.) analyzed for 0.54% N.

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2. A reaction product according to claim 1 wherein said acid material is an acid, amide or ester and said amino-alkanol has the formula

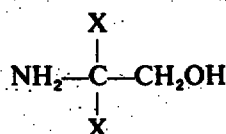


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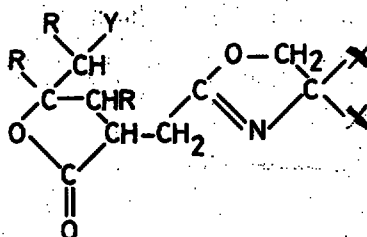
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wherein X is alkyl or hydroxyalkyl, said alkyl groups having 1 to 3 carbon atoms, and at least one of said X is a hydroxyalkyl group of the structure $-(\text{CH}_2)_n\text{OH}$ where n is 1 to 3.

3. A reaction product according to either of claims 1 and 2 wherein said hydrocarbon-substituted lactone acid material is polyisobutyl lactone carboxylic acid, said aminoalkanol is *tris*-(hydroxymethyl) aminomethane and said heating is continued until about 2 molar equivalents of water have evolved.

4. A reaction product according to any one of the preceding claims comprising a major proportion of lactone oxazoline represented by the formula:

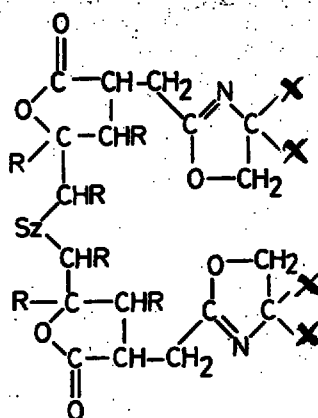


wherein R is hydrogen or an alkyl radical containing from 1 to 400 carbon atoms, X is alkyl or hydroxyalkyl and Y is hydrogen, hydroxyl, sulphonic acid, alkylthio, alkylidithio or a sulphur bridge containing 1 to 4 sulphur atoms and wherein said sulphur bridge is linked to a second lactone oxazoline group of said formula.

5. A hydrocarbonyl lactone oxazoline according to claim 4 wherein X is a hydroxyalkyl group of the structure $-(\text{CH}_2)_n\text{OH}$ wherein n is 1 to 3.

6. A reaction product according to any one of the preceding claims comprising a major proportion of polyisobutyl lactone - [5,5 - bis - (hydroxymethyl)oxazoline - 2].

7. A reaction product according to claim 4 wherein said sulphur bridge containing material is a thio-bis-(hydrocarbonyl lactone oxazoline) represented by the formula:



wherein z is an integer ranging from 1 to 4.

8. An oil or fuel composition comprising a lubricating oil or fuel oil and a lactone-oxazoline reaction product according to any one of the preceding claims.

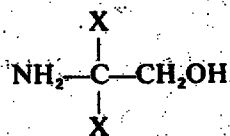
9. A process for preparing a lactone oxazoline according to any one of the preceding claims comprising heating together substantially equimolar amounts of an alkyl lactone carboxylic acid, amide or ester and a 2,2-disubstituted-2-amino-1-alkanol having 1 to 3 hydroxy groups and containing a total of 4 to 8 carbon atoms per molecule of the formula:

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wherein X is alkyl or hydroxyalkyl, said alkyl groups having 1 to 3 carbon atoms, provided at least one of said X is a hydroxyalkyl group of the structure $-(\text{CH}_2)_n\text{OH}$ where n is 1 to 3; at a temperature in the range of 100 to 240°C until infrared absorption is maximal indicating completion of the oxazoline reaction.

10. A lactone oxazoline reaction product according to claim 1 substantially as hereinbefore described with reference to the Examples.

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