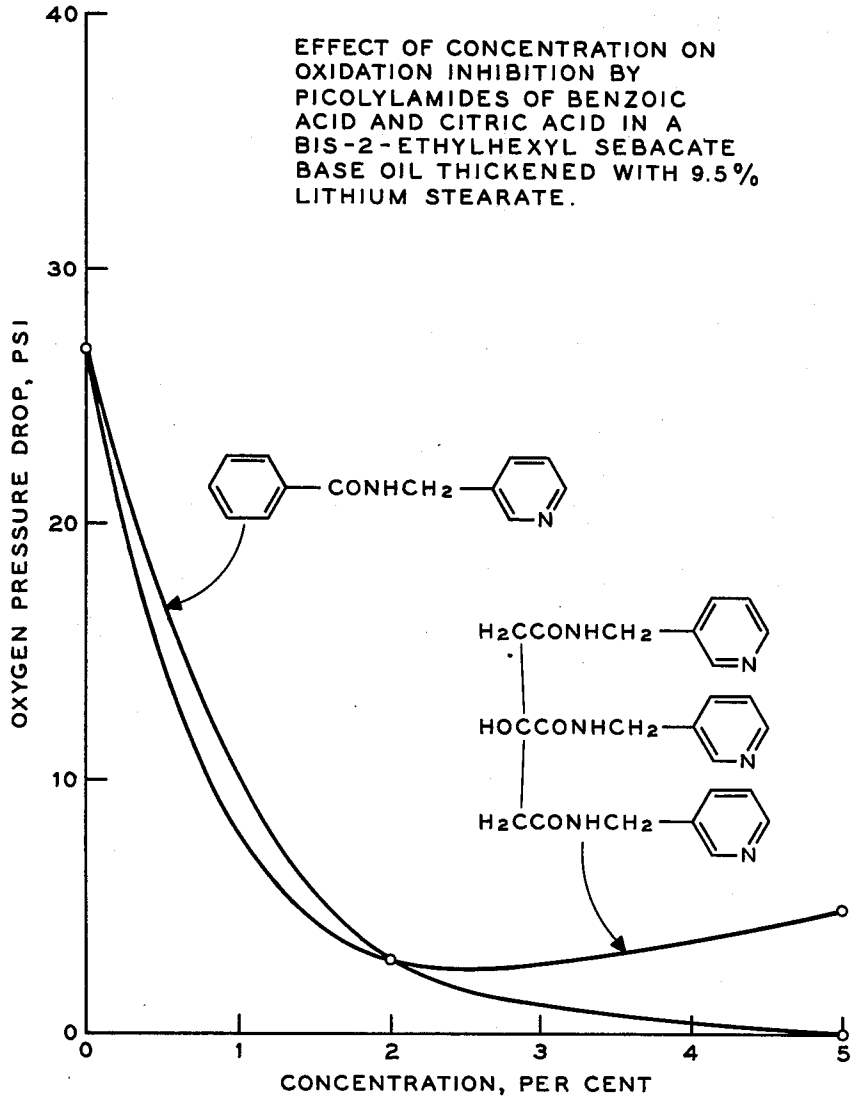
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OXIDATION RESISTANT GREASE COMPOSITIONS

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INVENTOR
BRUCE W. HOTTEN
BY P. C. Johnston
Raymond Sandrud

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OXIDATION RESISTANT GREASE COMPOSITIONS

Bruce W. Hotten, Orinda, Calif., assignor to Chevron Research Company, a corporation of Delaware

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The present invention pertains to new compounds which are particularly useful as oxidation inhibitors in oxidation susceptible media; for example, new compounds which are particularly useful as oxidation inhibitors in grease compositions.

The oxidation of lubricating oil compositions, for example, is detrimental to the wearing surfaces being lubricated. This is true not only of freely flowing lubricating oil compositions, but also to thickened lubricating oil compositions.

Subsequent to their manufacture, grease compositions are stored for relatively long periods of time prior to their use as a lubricant. During these periods of storage, ordinary grease compositions tend to oxidize, yielding oxidation products which are acidic in nature. Grease compositions oxidize not only in storage, but also during their use in the lubrication of wearing surfaces, forming products which are acidic in nature. The acidic products which are thus formed are detrimental to the metal surfaces to which the grease itself is finally applied. Even though such grease compositions may initially supply the necessary lubricity for wearing surfaces, such as ball and roller bearings, such wearing surfaces would be readily corroded due to the corrosive action of the oxidation products in the greases. Thus, although grease compositions can lubricate bearings and other wearing surfaces, the acidic products are detrimental, causing corrosive damage to the wearing surfaces. Also, sludging caused by oxidation is detrimental to the proper lubrication of wearing surfaces.

Although the deterioration of lubricating greases by oxidation is usually slow, the partial oxidation products formed in greases catalyze the oxidation and deterioration of greases until eventually a hard, crusty material which has no lubrication value whatsoever is formed. Also, such deterioration occurs much more rapidly in service than in storage, particularly since the metals such as copper and copper-lead alloys further catalyze the oxidation of grease compositions.

Modern usage and increasingly severe requirements make it necessary for grease compositions to have incorporated therein oxidation inhibitors which are effective to inhibit oxidation at normal storage temperatures and also at high service temperatures. Although many oxidation inhibitors, such as, for example, tertiary butyl phenol and hydroquinone, are available, they are volatile and evaporate from lubricating oil compositions at high temperatures.

The new compounds described herein effectively inhibit oxidation of grease compositions used at extremely high service temperatures and where the service requirements are severe.

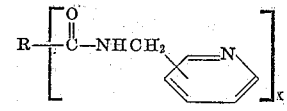
Therefore, it is an object of this invention to describe new compounds which are particularly effective for inhibiting oxidation of thickened lubricating oil compositions, such as greases.

In accordance with the present invention, it has been discovered that carboxylic acid amides of amino methyl pyridine are new compounds which are effective as oxidation inhibitors.

The oxidation inhibitors described herein effectively inhibit oxidation of grease compositions at high temperatures and at low temperatures.

The carboxylic acid amides of amino methyl pyridine

(also termed picolylamides for brevity) of the subject invention have the following generic formula:



wherein R is a hydrocarbon residue of a mono- or a polycarboxylic acid, and x is a number from 1 to 4. The R residue may be a cyclic or an acyclic radical. As a cyclic radical R may have from 5 to 30 carbon atoms, preferably 6 to 22 carbon atoms; that is, derived from cyclic carboxylic acids having from 6 to 31 carbon atoms, preferably, from 7 to 23 carbon atoms. As an acyclic radical, R may have from 0 to 36 carbon atoms, preferably from 2 to 10 carbon atoms; that is, derived from acyclic carboxylic acids having from 2 to 37 carbon atoms, preferably 3 to 10 carbon atoms. Thus R may be a hydrocarbon radical having from 0 to 34 carbon atoms.

When R is a cyclic radical, it is preferred that R is phenylene radical as exemplified by the isophthalic acid radical. Thus, x in the above formula is 2.

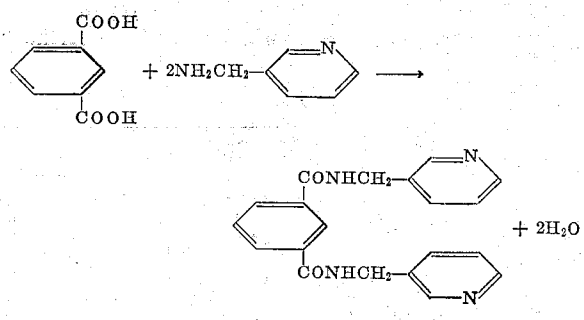
When R is an acyclic radical, it is preferred that R is an alkyl radical having from 2 to 3 carbon atoms, and that x has a value of 2 to 3.

When R in the formula hereinabove is a cyclic radical, such radicals can be derived from the carboxylic acids exemplified as follows: benzoic acid, isophthalic acid, etc.

When R in the generic formula is acyclic, the carboxylic acids from which R can be derived can be exemplified as follows: oxalic acid, glutaric acid, adipic acid, succinic acid, maleic acid, pimelic acid, subaric acid, azelaic acid, sebacic acid, citric acid, ethylene-dinitrilotetraacetic acid, aliphatic carboxylic acids, such as, acetic acid, butyric acid, hexanoic acid, decanoic acid, etc.

The new oxidation inhibitors described herein can be prepared by reacting a carboxylic acid with α-picoline, β-picoline, or γ-picoline in the proper mol ratio to provide 1 mol of picoline radical per carboxylic acid radical.

The reaction in the formation of the picolylamides described herein follows the equation set forth as follows, using isophthalic and 3-picolylamines as exemplifying the reactants:



Example I hereinbelow illustrates the preparation of the amides of picoline described herein as new compounds and useful as oxidation inhibitors in lubricating oil compositions.

Example I.—Preparation of the aminomethylpyridine amide of isophathalic acid

A mixture of 216 g. (2 mols) of 3-picolylamine and 244 g. (2 mols) of benzoic acid was heated at temperatures ranging from 150–220° C. for a period of 8 hours until the reaction has been completed as signaled by the evolution of 2 mols of water. The reaction product was purified by means of ethyl acetate as a solvent. The resulting 3-picolylamide of benzoic acid had a melting tem-

perature range of 96–99° C., and contained 6.52% basic nitrogen (theoretical=6.58%).

Lubricating oils which are suitable herein as base oils for the compositions of this invention include a wide variety of lubricating oils, such as naphthenic base, paraffin base and mixed base, other hydrocarbon lubricants, e.g., lubricating oils derived from coal products, and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc. and mixtures thereof), alkylene oxide type polymers, dicarboxylic acid esters, liquid esters of acids of phosphorus, numerous alkyl benzenes (polymers of silicon, polyphenyls (e.g., biphenyls and terphenyls), alkyl biphenyl ethers, etc.

Synthetic oils of the alkylene oxide type polymers which may be used include those exemplified by the alkylene oxide polymers (e.g., propylene oxide polymers), and derivatives, including alkylene oxide polymers prepared by polymerizing the alkylene oxides, e.g., propylene oxide, in the present of water or alcohols, e.g., ethyl alcohol, esters of ethylene oxide type polymers, e.g., acetylated ethylene oxide polymers prepared by acetylating ethylene oxide polymers containing hydroxyl groups; polyethers prepared from ethylene glycols, e.g., ethylene glycol, etc.

Synthetic oils of the dicarboxylic acid ester type include those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, subaric acid, sebacic acid, alkanol succinic acid, fumaric acid, maleic acid, etc., with alcohols, such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, etc. Examples of dibasic acid ester synthetic oils include dibutyl adipate, dihexyl adipate, and di-N-hexyl fumaric polymer.

Synthetic oils of the alkyl benzene type include those which are prepared by alkylating benzene, (e.g., dodecyl benzene, tetradecyl benzene, etc.).

Synthetic oils of the types of polymers of silicon include the liquid ester of silicon and polysiloxanes, which include those exemplified by tetraethyl silicate, tetraisopropyl silicate, tetra(4-methyl-2-penta) silicates, poly(methyl) siloxane, poly(methylphenyl) siloxane, etc.

The picolylamides, that is, the carboxylic amides of aminomethylpyridine can be used in oils in amounts of 0.1% to 10%, by weight, preferably, 1% to 5%, by weight. The drawing illustrates the effect of concentration of the picolylamides on oxidation inhibition of lubricating oil compositions.

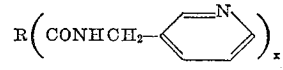
Grease thickening agents which can be used herein are those which can thicken the base oils to the consistency of the greases, which amounts are used from 5% to 30% by weight, more preferably from 7% to 20% by weight. Such grease thickening agents include: metal soaps of fatty acids (e.g., lithium stearate, calcium oleate, aluminum stearate, sodium hydroxystearate, calcium hydroxystearate), metal terephthalamates (e.g., sodium octadecyl terephthalamate), polyureas (e.g., tetraureas), metal alkane phosphonates (e.g., lithium octadecane phosphonate), etc.

Table I hereinbelow sets forth data showing the effectiveness of the picolylamides of this invention as oxidation inhibitors at 5% concentration in lubricating greases. The grease compositions were lithium base greases consisting of 15% lithium stearate in a bis-2-ethylhexyl sebacate base oil. As is well known, lithium soaps have an extremely pro-oxidative effect on grease compositions.

The "bearing life" of Table I was determined by the following test procedure, which is identified as the Navy High Speed Bearing Test. In the test, a ball-bearing packed with a grease was operated at 10,000 r.p.m. continuously for approximately 22 hours at 300° F. The apparatus was then cooled to room temperature during a period of 2 hours. This procedure of operation at 10,000 r.p.m. at 300° F. and cooling was repeated until there was bearing failure. The number of hours noted in the Table I for the high speed bearing life was the number of hours before bearing failure.

The bomb oxidation test value is the oxygen pressure drop in pounds per square inch during the 100 hours of the test.

The picolylamides used were those of the formula



wherein R is the residue of the carboxylic acid set forth in Table I, and x is a number from 1 to 4 equal to the number of carboxylic acid radicals in the carboxylic acid reactant.

TABLE I

Parent Acid of 3-Picolylamide	Bomb Oxidation Pressure Drop, p.s.i.	Bearing Life (Hours) Avg. of 3 Tests
None (Base Grease)	27	222
Benzoic	0	397
Succinic	3	405
Maleic	11	600
Isophthalic	5	370
Tartaric	4	583
Citric	6	155
Ethylenedinitrilotetraacetic	14	312

Table II hereinbelow summarizes the preparation of numerous 3-picolylamides of carboxylic acids described herein, including the physical properties of the resulting amides.

TABLE II

Composition	A	B	C	D	E	F	G
3-Picolylamine, g. (mols)	216(2)	216(2)	216(2)	324(3)	432(4)	324(3)	432(4)
Benzoic Acid, g. (mols)	244(2)						
Succinic Acid, g. (mols)		118(1)					
Maleic Anhydride, g. (mols)			98(1)				
Isophthalic Acid, g. (mols)				249(1.5)			
A-Tartaric Acid, g. (mols)					300(2)		
Citric Acid, g. (mols)						192(1)	
Ethylenedinitrilotetraacetic acid, g. (mols)							292(1)
Temperature, °C	150–220	150–170	140–200	130–220	90–150	70–150	150–200
Time, Hours	8	2	5	12	2	2	.7
Melting Temperature, ° C	96–99	196–203	294–298	157–160	203–209	Resinous	130–132
Analysis:							
(a) Basic Nitrogen, percent—							
Found	6.52	9.35	9.5			9.18	
Calculated	6.58	9.4	9.5			9.13	
(b) Nitrogen, percent—							
Found		19.0		16.3	17.0	17.1	21.6
Calculated		18.8		16.2	17.0	18.2	21.5

In addition to the oxidation inhibitors described herein, the grease compositions may contain rust inhibitors, extreme pressure agents, oiliness agents, etc.

I claim:

1. A grease composition subject to oxidative deterioration containing in an amount sufficient to inhibit oxidation a carboxylic amide of aminomethyl pyridine, wherein said carboxylic acid is selected from the group consisting of hydrocarbon carboxylic acids of not more than 34 carbon atoms and of 1–4 carboxylic groups, tartaric acid, citric acid and ethylenedinitrilotetraacetic acid.

2. A composition according to claim 1 wherein said grease contains as a grease thickening agent from 5 to 30 weight percent of a metal soap of a fatty acid.

3. A grease composition subject to oxidative deterioration containing from 5 to 30 weight percent of a metal soap of a fatty acid and in an amount sufficient to inhibit oxidation the benzamide of aminomethyl pyridine.

4. A great composition subject to oxidative deterioration containing from 5 to 30 weight percent of a metal soap of a fatty acid and in an amount sufficient to inhibit oxidation the maleamide of aminomethyl pyridine.

5. A grease composition subject to oxidative deterioration containing from 5 to 30 weight percent of a metal soap of a fatty acid as a grease thickening agent and in an amount sufficient to inhibit oxidation the succinamide of aminomethyl pyridine.

6. A grease composition subject to oxidative deterioration containing from 5 to 30 weight percent of a metal soap of a fatty acid as a grease thickener and in an amount sufficient to inhibit oxidation the tartaramide of aminomethyl pyridine.

7. A grease composition subject to oxidative deterioration containing from 5 to 30 weight percent of lithium stearate as a grease thickening agent and in an amount sufficient to inhibit oxidation the maleamide of aminomethyl pyridine.

8. A grease composition subject to oxidative deterioration containing from 5 to 30 weight percent of lithium stearate as a grease thickening agent and in an amount sufficient to inhibit oxidation the tartaramide of aminomethyl pyridine.

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DANIEL E. WYMAN, *Primary Examiner.*