

[54] LUBRICATING OIL COMPOSITION  
CONTAINING ANTI-WEAR AGENTS

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[56] References Cited

UNITED STATES PATENTS

2,483,800 10/1949 Zimmer et al. .... 252/33.4

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793,684 4/1958 Great Britain ..... 252/18

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[57] ABSTRACT

Lubricating Oil compositions are provided comprising (a) an oil of lubricating viscosity, (b) an effective amount of a dispersing agent and (c) a nitrate of a Group I or Group II metal in an amount effective to substantially reduce wear. The lubricating oil compositions are useful for, among other things, reducing the wear in internal combustion engines, particularly in high power output engines such as locomotive engines and the engines used to propel ocean going vessels.

12 Claims, No Drawings

# LUBRICATING OIL COMPOSITION CONTAINING ANTI-WEAR AGENTS

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

This invention relates to lubricating oil compositions, particularly to lubricating oil compositions useful to reduce the wear occurring between relatively moving parts such as in the crankcase and between the piston rings and cylinder walls of internal combustion engines.

Wear always has been a continuing problem associated with relatively moving parts. To effect a reduction in such wear, relatively moving parts have been lubricated by various means throughout recorded history. Various types of lubricants such as animal fats have been used. Later compounded versions of naturally occurring fats and oils were used. Eventually technology progressed to the point where today highly compounded mineral oil and synthetic compound based lubricants are available for lubricating relatively moving parts. However even with these highly compounded lubricants which provide markedly reduced wear, the problem is far from being solved. Appreciable rates of wear still occur in almost any circumstance where relatively moving parts are found. Examples of high rates of wear are found in the crankcase bearings and on piston ring and cylinder wall surfaces of internal combustion engines. Particularly high rates of wear occur in high output engines such as diesel locomotives and ocean going vessel diesel engines (hereinafter referred to as marine engines) especially when these engines are operated on fuels containing appreciable amounts of sulphur.

### 2. Description of the Prior Art

Water-in-oil emulsions suitable for lubricating engines such as low speed diesel engines operating on high sulfur fuels are disclosed in Stillebroer et al. U.S. Pat. No. 2,744,870 issued May 8, 1956. These water-in-oil emulsions contain from about five to about forty per cent water and a water soluble salt of a divalent material.

A process for reacting ions of an acidic material with basic metal-containing organic complexes whereby the anions are incorporated in the metal-containing complexes is disclosed in Le Suer, U.S. Pat. No. 3,496,105, issued Feb. 17, 1970. An example is the reaction of the anions of an inorganic acid with a basic, carbonated Group II metal-containing complex to incorporate the anions into the reaction product. The process is conducted by contacting the complex with the anions of the acidic material in a suitable medium until at least a portion of the anions react with the metal. The process is conducted in the presence of at least one peptizing agent. The products are useful, inter alia, as additives for lubricating oils.

Le Suer U.S. Pat. No. 3,515,669, issued June 2, 1970 discloses a process for preparing Group I and Group II metal dispersions in essentially inert diluents by contacting a Group I or Group II basically reacting metal compound with an acidic material in the presence of a stabilizing agent and a promoter. Preferred basic reacting compounds include Group I and Group II metal oxides, hydroxides and alkoxides. Promoters include phenols, alcohols and nitroalkanes. Stabilizing agents include esters, amides, imides and amidine derivatives of organic acids. Preferred acidic materials are inorganic acids or inorganic acid gases. The metal-containing dis-

persions obtained are useful as additives for fuels and lubricants.

A process for the preparation of suspensions of water soluble solids in oleaginous media such as hydrocarbons in which the solids are insoluble is disclosed in Blake, U.S. Pat. No. 3,013,968, issued Dec. 19, 1961. The process involves forming an emulsion from an aqueous solution of the solid and the oleaginous liquid. The water-in-oil emulsion is obtained by using petroleum wax oxidate as the emulsifier. Emulsion is thereafter dehydrated.

Blake et al., U.S. Pat. No. 3,065,173, issued Nov. 20, 1962 describes a process for dispersing water soluble solids in the oleaginous material. In this patent the emulsifying agent is montan wax. Blake et al., U.S. Pat. Nos. 3,065,174; 3,065,175 and 3,065,176, all of the same issue date, disclose the use of other emulsifiers in the same process.

Oil soluble basic metal salts of organic acids which can be obtained by the reaction of such acids with an excess amount of a metal base in the presence of an acidic gas and a promoter under substantially anhydrous conditions are described in Norman et al., U.S. Pat. No. 3,595,790, issued July 27, 1971. The promoters are organic hydroxy compounds in which the hydroxy group is bonded to a non-benzenoid carbon atom. The inorganic acid material can be a strong or weak acid or the anhydride gas of the acid.

Cutting fluids for machining ferrous materials are shown in Compton U.S. Pat. No. 3,215,630, issued Nov. 2, 1965. These cutting fluids are aqueous salt solutions. Useful salts are those having specified cation-anion radius ratios. The particular ranges of radius ratios useful depend on the anions of the salt. Salts which have radius ratios falling outside this specified range fail to cover the faces of the alpha iron crystals on the ferrous stock and therefore do not provide suitable cutting fluids.

## SUMMARY OF THE INVENTION

The lubricating oil compositions of this invention comprise (a) an oil of lubricating viscosity, (b) an effective amount of a dispersing agent, preferably selected from hydrocarbyl nitrogenous dispersants, Group I and Group II metal-containing dispersants, and mixtures thereof, and (c) a nitrate of a Group I or Group II metal in an amount effective to substantially reduce wear.

The lubricating oil compositions of the invention are useful for reducing the wear between relatively moving parts. The compositions are particularly valuable since they provide wear protection for engines operated on high sulfur content fuels and/or under conditions of high power output.

## DESCRIPTION OF THE INVENTION

As described above the lubricating oil composition of the invention comprises an oil of lubricating viscosity, an effective amount of a dispersing agent and a nitrate of a Group I or Group II metal.

### The Dispersant Component

The dispersants are present to, among other things, maintain the nitrate dispersed throughout the lubricating oil. A variety of dispersants are suitable for use in this invention. As discussed above the dispersants are preferably selected from hydrocarbyl nitrogenous dis-

persants and Group I and Group II metal-containing dispersants and mixtures thereof.

The Group I and Group II metal containing dispersants are well known in the art. These dispersants are salts of Group I and Group II metals in which the anionic portion of the salt contains an oil solubilizing group.

The oil solubilizing group generally has at least 9 and usually 12 to 18 or more carbon atoms, preferably from about 12 to 200 carbon atoms. The oil solubilizing groups are usually but not necessarily hydrocarbyl groups. The hydrocarbyl groups are organic radicals composed of carbon and hydrogen except for minor, sometimes adventitious, amounts of other elements, such as oxygen, chlorine, etc. The term denotes an aliphatic or aromatic radical, or a radical which is a combination thereof, e.g., aralkyl. Preferably, the hydrocarbyl group will be relatively free of aliphatic unsaturation, i.e., ethylenic and acetylenic, particularly acetylenic. The hydrocarbyl substituents will contain 30 carbon atoms and preferably 200 carbon atoms. When the hydrocarbyl groups are of lower molecular weight, the average number of hydrocarbyl substituents in a given dispersant may be greater than one. The hydrocarbyl groups are preferably aliphatic, having preferably from 0 to 2 sites of ethylenic unsaturation and most preferably from 0 to 1 such site. Hydrocarbyl groups derived from a polyolefin, itself derived from olefins (normally 1-olefins) from 2 to 6 carbon atoms (ethylene being copolymerized with an olefin of at least 3 carbon atoms), or from a high molecular weight petroleum-derived hydrocarbon, are preferred, and of these, polyisobutylene is most preferred.

Illustrative sources for the high molecular weight hydrocarbyl substituents are petroleum mineral oils such as naphthenic bright stocks, polypropylene, polyisobutylene, poly-1-butene, copolymers of ethylene and isobutylene, polypropylene and isobutylene, poly-1-pentene, poly-4-methyl-1-pentene, poly-1-hexene, and poly-3-methylbutene-1, etc.

The acid reacting functional group can be a variety of well known groups which include the sulfonic acid group, the hydroxy group (usually in the form of a phenol) and the carboxylic acid group. These groups, when in the form of the metal salts are known as sulfonates, alcoholates (phenates), and carboxylates, respectively.

These Group I and Group II metal containing dispersants can be used alone or in mixtures. Particularly good results are obtained from sulfonates, phenates and mixtures thereof.

The term sulfonates is intended to encompass the salts of sulfonic acids derived from petroleum products. Such acids are well known in the art. They are prepared by treating petroleum products with sulfuric acid or  $\text{SO}_3$ . The compounds in the petroleum product which become sulfonated contain an oil solubilizing group as discussed above. The acids thus obtained are known as petroleum sulfonic acids and the salts as petroleum sulfonates. Also included within the meaning of sulfonates are the salts of sulfonic acids of synthetic alkylaryl compounds. These acids are prepared by treating an alkylaryl compound with sulfuric acid or  $\text{SO}_3$ . At least one alkyl substituent of the aryl compound is an oil solubilizing group as discussed above. The acids thus obtained are known as alkylaryl sulfonic acids and the salts as alkylaryl sulfonates. The sulfonates wherein the

alkyl is a straight-chain alkyl are the well known linear alkyl sulfonates (LAS). The acids are then converted to the metal salts thereof by neutralization with a basic reacting alkali or alkaline earth metal compound to yield the Group I or Group II metal sulfonate. Generally the acids are neutralized with an alkali metal base. If an alkaline earth metal salt is desired, it is prepared from the alkali earth metal salt by metathesis. Alternatively, the sulfonic acid may be neutralized by direct reaction with an alkaline earth metal base.

The sulfonates can be overbased. Overbased materials are characterized by a metal content in excess of that which would be present according to the stoichiometry of the metal cation and the particular organic compound said to be overbased. Thus an oil soluble monosulfonic acid when neutralized with a Group II basic metal compound, e.g., a calcium compound, will produce a normal sulfonate containing one equivalent of calcium for each equivalent of acid. In other words the normal metal sulfonate will contain one mol of calcium for each two mols of the monosulfonic acid.

By applying well-known procedures "overbased" or "basic" complexes of the sulfonic acids can be obtained. These overbased materials can contain amounts of metal many times in excess of that required to neutralize the acid. These stoichiometric excesses can vary considerably, e.g., from about 0.1 to about 30 or more equivalents depending upon the reactants, the process conditions, etc.

The degree of overbasing can be expressed several ways. One method is to describe the "metal ratio." This method describes the ratio of the total chemical equivalents of metal in the product to the chemical equivalents of the compound said to be overbased, based on the known chemical reactivity and stoichiometry of the two reactants. Thus in a normal (neutral) calcium sulfonate, the metal ratio is 1 and in overbased sulfonate the metal ratio can range from about 1.1 to 30 or more, generally from about 5 to 25.

Another method of expressing the degree of overbasing is to describe the "base ratio." This method describes the ratio of chemical equivalents of basic metal to the chemical equivalents of neutral metal. The neutral metal is the metal which would be expected to react with the compound to be overbased, i.e., the metal required to neutralize the sulfonate, phenate or carboxylate. The basic metal is the metal in excess of the neutral metal, i.e., it is the metal available to neutralize acidic combustion products. Thus a normal (neutral) calcium sulfonate has a base ratio of 0 and an overbased sulfonate can have a base ratio ranging from about 0.1 up to about 30 or more, generally from about 4 to about 24.

Another method of specifying the degree of overbasing of dispersants such as the sulfonates is by stating the alkalinity value (AV) of the composition. The method for determining the alkalinity value of an overbased composition is set forth in ASTM Method D-2896. Briefly, the alkalinity value is stated as the number of milligrams of potassium hydroxide per gram of composition to which the overbasing is equal. For example if the composition is overbased to the extent that it has the same acid neutralizing capacity per gram as 10 milligrams of potassium hydroxide, the composition is given an alkalinity value of 10. Alkalinity values can range up to about 600. Of course the lower limit is zero for a neutral sulfonate, with values of 10 to 50 being

common for slightly overbased sulfonates. Highly overbased sulfonates have values ranging from about 275 to about 450.

A discussion of the general method of preparing overbased sulfonates and other overbased products is disclosed in Le Suer U.S. Pat. No. 3,496,105, issued Feb. 17, 1970 particularly at columns 3 and 4.

The term phenates encompasses Group I and Group II metal salts of phenolic compounds which are substituted with an oil solubilizing group.

The phenates can be overbased also. Techniques for producing these overbased complexes are well known, many of which are set forth in the above-mentioned Le Suer patent.

The term carboxylates encompasses the salts of carboxylic acids. Acids which are useful in the instant invention generally contain at least 12 carbon atoms, e.g., palmitic, stearic, myristic, oleic, linoleic, etc. acids. Other carboxylic acids include the cyclic acids. Among these are acids containing an aryl group, ie. benzene, naphthalene, etc., substituted with an oil solubilizing radical or radicals having a total of at least 15 to 18 carbon atoms or more, e.g., alkylbenzoic acid, alkylnaphthanoic acid, alkylsalicylic acid, etc. Preferably the cyclic acids are those which contain a cycloaliphatic group substituted with an oil solubilizing group. Examples of such acids are the petroleum naphthenic acids, e.g., cetylcyclohexane carboxylic acid, dilauryldecahydronaphthalene carboxylic acid, etc. Of the above acids, the petroleum naphthenic acids are preferred. The salts of this preferred class of cycloaliphatic acids are commonly known as naphthenates.

The sulfonates, phenates and carboxylates are present in the lubricating oil composition in the form of their Group I and Group II metal salts. Group I metals useful in forming the dispersing agent include lithium, sodium and potassium. Group II metals useful in forming the dispersing agent include magnesium, calcium and barium of which calcium is preferred.

The hydrocarbyl nitrogenous dispersants are a well known class of ashless dispersants. This class of dispersants include hydrocarbyl-substituted amines, amides and cyclicimides in which the hydrocarbyl group or groups act as the oil solubilizing group as discussed above.

The hydrocarbyl-substituted amines are derived from ammonia, monoamines and polyamines. Examples of the amines include ethyl amine, butyl amine, piperazine, and alkylene polyamines and preferably polyalkylene polyamides such as ethylene diamine, 2-aminoethyl piperazine, diethylene triamine, trimethylene diamine, di(trimethylene) triamine, dipropylene triamine, triethylene tetramine, tripropylene tetramine, tetraethylene pentamine, pentaethylene hexamine, etc. These amines encompass alkyl-substituted amines, e.g., N-methylethylene diamine, N,N'-dimethylethylene diamine, N,N-dimethylpropylene diamine, N-hydroxyethylethylene diamine, etc. Amines having up to about 12 amino nitrogens are especially preferred. The hydrocarbyl-substituted amines are prepared, in general, by reaction of a halogen-substituted hydrocarbon with the amine. Details of such preparations are further descriptions of some of these hydrocarbyl-substituted amines can be found in Honnen and Anderson U.S. Pat. Nos. 3,565,804 and 3,438,757.

The hydrocarbyl-substituted amides and cyclicimides are derived from the reaction of hydrocarbyl-

substituted carboxylic acids, anhydrides, acid chlorides, etc., with certain of the amines described above. A preferred dispersant is the reaction product of hydrocarbyl-substituted succinic acid or anhydride with amines containing at least one primary or secondary amino nitrogen, e.g., the polyalkylene polyamines fulfill this requirement as do the substituted polyalkylene polyamines, and for that matter, ammonia.

The bis-succinimides also find use in this invention. The bis-succinimides are prepared by the reaction of hydrocarbyl-substituted succinic acid or anhydride with an amine containing at least two primary and/or secondary nitrogens. Such bis-succinimides are, for example, the polyisobutenyl bis-succinimides of ethylene diamine, diethylene triamine, or triethylene tetramine, or tetraethylene pentamine or N-methyldipropylene triamine, etc. (e.g., Benoit, U.S. Pat. No. 3,438,899).

The various above-described dispersing agents can be used alone or in mixtures.

The dispersing agent will be present in amounts ranging from about 0.001 to 10.0 per cent in compositions of the invention prepared for use as the actual lubricating oil composition. Concentrates of lubricating oil additives are often prepared. These concentrates are then later blended with an oil of lubricating viscosity to yield the final lubricating oil composition which will ultimately be used to lubricate relatively moving parts. The amount of dispersing agent contained in concentrates of the compositions of this invention can be quite high; for example, up to about 50 per cent or more, generally from about 5 to about 30 per cent.

Since the compositions of this invention will in most cases be used in combination with other lubricating oil additives such as overbased dispersants it is generally not necessary that the compositions be highly overbased. The overbased dispersants with which the compositions of this invention will be used will normally supply the necessary reserve alkalinity of the oil. However, for convenience the dispersing agents can contain a high degree of overbasing thereby avoiding the necessity of further compounding the lubricating oil composition to give it the desired properties.

#### The Nitrate Component

In addition to the dispersing agent discussed above the lubricating oil compositions of this invention contain a nitrate of a Group I or Group II metal in an amount effective to substantially reduce wear. The Group I or Group II metals of the nitrate are the same as discussed above for the dispersing agent namely lithium, sodium, potassium, magnesium, calcium and barium. Preferably the Group I and Group II metals are sodium and calcium.

The quantity of nitrate present in the lubricating oil composition can vary widely. For example, the quantity of nitrate can be as little as 135 parts per million or less (based on nitrate) in the finished compounded lubricating oil composition. In general finished lubricating oil compositions will contain from about 135 parts per million to about 3,000 parts per million (based on nitrate) of the Group I or Group II metal nitrates. Preferably the finished lubricating oil compositions will contain from about 180 to about 1,100 parts per million (based on nitrate) of the Group I or Group II metal nitrates. Concentrates of a Group I or Group II metal nitrate can contain from about 1 to about 55 weight per cent of the nitrate. Preferably the concentrates contain

from about 2 to about 50 weight per cent of the nitrate. Concentrates containing greater amounts of the nitrate have the advantages of reduced transportation costs, reduced storage requirements, etc. since less of it will be required to be blended into a lubricating oil to produce the finished composition. For these reasons concentrates preferably contain about 20 to about 50 per cent of the nitrate.

In most cases the higher concentrations of the nitrate are preferred. However, combinations of certain nitrates with certain dispersing agents produce somewhat unstable dispersions and a certain amount of the nitrate will settle out in the form of sediment during prolonged storage thereby making compounding more difficult. This problem seems to occur most often with Group I metal nitrates. In these cases it is often desirable to limit the concentration of the nitrate to the lower end of the ranges specified above.

#### The Lubricating Oil

The lubricating oil composition of the invention contains an oil of lubricating viscosity. This oil can be any oil suitable for lubricating purposes. It is generally a lubricating oil fraction of petroleum, either naphthenic or paraffinic base, unrefined, acid refined, or solvent refined as required in the particular lubricating need. Also, synthetic oil meeting the necessary viscosity requirements, either with or without a viscosity index improver may be used as the base stock.

The viscosity of the lubricating oil will vary greatly depending upon the use to which it is to be put. It is well within the skill of those in the art to tailor the lubricating oil composition to the desired viscosity specifications by choosing the appropriate base stock, mixing various base oils, and/or compounding these oils or mixtures thereof with various viscosity index improving agents commercially available.

#### The Process of Preparing the Lubricating Oil Compositions

One process for preparing the lubricating oil compositions of the invention comprises contacting a lubricating oil composition containing a Group I or Group II metal containing sulfonate, phenate, carboxylate or mixtures thereof and having dispersed therein a basic reacting Group I or Group II metal compound, with an amount of nitric acid not greater than that required to react with the Group I or Group II metal present in excess of the metal required to stoichiometrically combine with the sulfonate, phenate or carboxylate anions. This process is the invention of R. E. Crocker and is disclosed and claimed in U.S. patent application Ser. No. 268,278 filed on even date herewith and entitled "Process for Preparing Lubricating Oil Compositions Containing Anti-Wear Agents."

The Group I or Group II metal containing sulfonates, phenates, and carboxylates are the same compounds as those described above under the heading dispersing agents. The basic reacting Group I or Group II metal compound dispersed in the lubricating oil composition can be any such basic reacting compound. However, for convenience these compounds generally are the type of basic reacting compounds found in the overbased sulfonate and phenate dispersants discussed above. Such compounds include oxides, hydroxides and carbonates of the Group I and Group II metals. Preferably the metal of the basic reacting compound is the same as the metal of the dispersant.

The amount of nitric acid used in the process is an amount not greater than that required to react with the Group I or Group II metal present in the composition which is in excess of the metal required to stoichiometrically combine with the sulfonate, phenate or carboxylate anions. The excess Group I or Group II metal present in the composition is that amount of metal which causes what is known as overbasing of the dispersing agent. It is important that the amount of nitric acid used not be greater than required to react with the excess Group I or Group II metal. If a larger amount of nitric acid should be used the dispersing agent may be attacked by the acid converting its Group I or Group II metal into a nitrate and liberating the anionic portion of the dispersing agent as the corresponding protonated compound. Should this occur the effective amount of dispersing agent in the lubricating oil composition will be correspondingly reduced.

The dispersing agent is present in the finished lubricating oil composition to maintain the nitrate in a dispersed state in the lubricating oil. If the amount of dispersing agent is reduced the quantity of nitrate which can be maintained satisfactorily dispersed in the lubricating oil composition is reduced. This can lead to sedimentation of the nitrate particularly when the composition contains high concentrations of the nitrate. Such sedimentation can cause difficulties when the concentrates are blended with a lubricating oil. Among other problems sedimentation can cause the plugging of pumps, lines, filters and the formation of deposits in storage tanks. Furthermore, quality control of the finished product becomes an extremely difficult, if not impossible task. Also the finished product is quite likely to be hazy rather than clear and bright.

The nitric acid added to the lubricating oil composition containing the dispersing agent and the basic reacting Group I or Group II metal compound will be an aqueous solution of the nitric acid. Addition to the oleaginous composition is accompanied by vigorous stirring. The addition can be accomplished at temperatures ranging from ambient temperature up to about 175°C or greater. If the nitric acid is added to the reaction mass at lower temperatures the water from the nitric acid itself as well as the water formed during the reaction are removed by later heating the reaction mass to a temperature great enough to evaporate off the water (conveniently about 150°C) while maintaining vigorous agitation. If the reaction mass is maintained above the boiling point of water during acid addition, the water will be removed from the reaction mass as it is introduced and formed.

While not necessary, it is preferred the nitric acid addition to the lubricating oil composition be carried out in the presence of an inert diluent. The inert diluent promotes contact between the nitric acid and the basic reacting metal compound. Although any inert diluent can be used, low boiling hydrocarbon fractions are preferred because of the ease with which they may be removed from the lubricating oil composition upon completion of the preparation. Examples of useful diluents include hexane, heptane, naphtha and the like.

The amount of diluent used can vary widely. The lower limit is of course zero when no diluent is used up to any convenient factor of dilution such as 10 or 20 parts of diluent per part of overbased lubricating oil composition. Generally there will be from 1 to 5 parts of diluent per part of oil composition.

Generally subsequent to acid addition and water removal, the oil composition is filtered to remove any nondispersed materials prior to the removal of all of the diluent filter aids such as the diatomaceous earths have been found useful in producing a clear, bright finished product.

The quantity of basic reacting Group I or Group II metal compound present in the compositions containing a dispersing agent contributes to the alkalinity value of the lubricating oil composition. It will be obvious that the greater the alkalinity value of the composition prior to being contacted with the nitric acid the larger is the amount of basic reacting Group I or Group II metal compound present. The larger the amount of such compound that is present in the composition the greater is the amount of nitrate that can be formed in situ. The capability to form large amounts of nitrate in situ is particularly advantageous when it is desired to prepare concentrates for blending with other lubricating oils. Therefore while lubricating oil compositions having alkalinity values of from about 6 to 10 prior to being contacted with nitric acid are suitable for use in the processes of this invention, lubricating oil compositions having alkalinity values of from about 50 to about 600 are preferred when concentrates of the nitrate are to be prepared in situ in the lubricating oil composition.

An alternative method of preparing lubricating oil compositions containing a Group I or Group II metal nitrate comprises adding an aqueous solution of the nitrate to a lubricating oil composition containing one or more dispersing agents. The addition is accompanied with vigorous agitation. Subsequent to or concurrent with the addition of the aqueous solution, the mixture is heated sufficiently to drive off the water such as described above for the in situ preparation of the nitrate. This method of preparation has found particular utility in the incorporation of Group I metal nitrates into a lubricating oil composition containing the hydrocarbyl succinimides or the Group II metal dispersing agents. It has also been found that this method is not as satisfactory as the in situ method of incorporating the Group II metal nitrates into the lubricating oil composition.

The aqueous solution of the nitrate can contain other materials such as other inorganic salts in addition to the Group I or Group II metal nitrate. Such materials include Group I and Group II metal silicates, borates, metaborates, nitrites and the like.

A phenomenon not yet understood is the tendency of lubricating oils containing the nitrates as described hereinabove to be sensitive to oxidation at elevated temperatures. The degree of sensitivity varies according to the base oil and the other additives present in the oil. For this reason, it is preferred that the lubricating oils of the invention contain an oxidation inhibitor. The only requirement for the oxidation inhibitor is that it be compatible with the nitrate and the other additives present in the composition. In particular, the oxidation inhibitor should not have a tendency to cause increased wear. Useful inhibitors include alkylphenates, sulfurized alkylphenates, amine substituted-sulfurized alkyl-

phenates, hindered phenols, especially the 2,5-di-tert-butyl-1-phenols, the zinc dihydrocarbyldithiophosphates and the like.

In addition to the dispersing agent and the Group I or Group II metal nitrate the lubricating oil compositions of the invention can contain a variety of other compounding agents such as other dispersants, detergents, extreme pressure agents, viscosity index improvers, and other materials known to be useful in compounding lubricating oils to meet the various exacting specifications demanded by the particular use to which the lubricating oil is to be put.

The following examples are incorporated for a further understanding of the invention.

#### EXAMPLE I.

To 367.5 grams of Dispersant 2 (see Table II of Example II below) in a Waring blender was added an aqueous solution comprised 9.7 grams of sodium nitrate, 7.15 grams of sodium nitrite and 45 grams of water. Vigorous agitation was supplied while the mixture was heated to 150°C to evaporate the water. The dehydrated product contained 2.5 percent w sodium nitrate and 1.9 percent w sodium nitrite.

Using the same procedure other dispersions of sodium nitrate and sodium nitrite, each alone or mixtures thereof, comprising from about 2 to about 5 percent of the finished composition were prepared and tested as shown in example II below.

#### EXAMPLE II.

The engine crankcase of a diesel powered railroad locomotive was charged with the required quantity of a commercially available diesel engine lubricating oil. The oil carried the engine manufacturer's approval for use in the engine.

The engine was equipped with radioactive piston rings. This allowed the wear of the rings to be established by measuring the radioactivity present in the oil rather than by disassembly of the engine. The engine was run to break in the rings, after which the crankcase was flushed with oil.

After being charged with the commercially available oil, the engine was run at full speed and full load for 8 hours to establish a reference wear rate. After 8 hours, the additive was added to the crankcase with the engine still running at full load and speed. The run was then continued for an additional 8 hours to determine the wear rate for the oil containing the additive. After each run, the crankcase was drained, flushed and refilled with a fresh charge of the base oil.

In some tests, the additive was added to the crankcase as a concentrated aqueous solution. Sump temperatures were high and the oil was circulated to the underhead of the pistons to cool them. The absence of free water in the oil demonstrated that the water boiled off leaving the additive dispersed in the oil.

In other tests the additive was dispersed in oil prior to addition to the crankcase. The dispersants used are described in footnotes to Table I below.

In Table I the wear is described as a percentage of the wear obtained with the reference oil.

TABLE I.

WEAR RESULTS OF RADIOACTIVE LOCOMOTIVE RING WEAR TEST

Component	Method of Addition	Use Level ppm anion	Fuel, Sulfur wt. %	Ring Face Material	Wear
mixture 1 <sup>(a)</sup>	Aqueous	458 (NO <sub>3</sub> )	0.5	Chrome	49
mixture 1	do.	458 (NO <sub>3</sub> )	0	do.	46
NaBO <sub>2</sub>	Dispersant 1 <sup>(b)</sup>	1860	0	do.	91

TABLE I.-Continued

WEAR RESULTS OF RADIOACTIVE LOCOMOTIVE RING WEAR TEST					
Component	Method of Addition	Use Level ppm anion	Fuel, Sulfur wt. %	Ring Face Material	Wear
NaNO <sub>2</sub> /NaNO <sub>3</sub> <sup>(a)</sup>	Aqueous	990/1370	0.12	Chrome	51
mixture 1	do.	458 (NO <sub>3</sub> )	0.5	Iron	60
NaNO <sub>2</sub> /NaNO <sub>3</sub>	do.	395/345	do.	do.	87
do.	Dispersant 2 <sup>(c)</sup>	375/520	do.	do.	134
do.	do.	do.	do.	do.	134
NaNO <sub>2</sub>	do.	338	do.	do.	219
NaBO <sub>2</sub>	Dispersant 3 <sup>(d)</sup>	450	do.	do.	100
do.	do.	1020	do.	do.	139
NaNO <sub>3</sub>	Dispersant 2	197	do.	do.	120
do.	do.	205	do.	do.	76
do.	do.	313	do.	do.	97
do.	do.	462	do.	do.	65
do.	do.	567	do.	do.	73
do.	do.	917	do.	do.	80

<sup>(a)</sup> Mixture 1 - an aqueous solution of sodium salts comprised of the following anions: silicate 3.8 % w, metaborate 39.2 % w, nitrite 16.5 % w and nitrate 17.0 % w

<sup>(b)</sup> Dispersant 1 - a polyisobutenylsuccinimide of tetraethylenepentamine, approximately 44% active dispersant in an oil solution.

<sup>(c)</sup> Dispersant 2 - a mixture of 81 % w of a sulfurized calcium polypropylenephenate (3.1% calcium) and 19 % w of an oil solution of a calcium sulfonate having an AV=5-8 (1.6% calcium)

<sup>(d)</sup> Dispersant 3 - a calcium sulfonate having an AV=5-8 (1.6% calcium in an oil solution)

<sup>(e)</sup> 49.3 % w sodium nitrate and 50.3 % w sodium nitrite

As can be seen from the above data most oils incorporating sodium nitrate gave appreciable reductions in wear relative to the wear experienced with the commercially available oil. It is not understood why the combination of sodium nitrite and nitrate when added as an oil dispersion in Dispersant 2 gave increased wear while the same combination when added as an aqueous solution gave reduced wear and sodium nitrate alone in the same dispersant also gave reduced wear. It will be noted that the metaborate gave little or no reduction in wear and in one case was harmful.

#### EXAMPLE III.

Following the procedure of Example I, dispersions of sodium nitrate in Dispersant 3 or a mixture of Dispersants 1 and 3 of Example II were prepared. These dispersions contained between 21 and 50 percent w sodium nitrate. Upon prolonged storage (several weeks), an objectionable amount of sediment formed in the dispersions having a high nitrate content. To avoid this these dispersions must be compounded into finished lubricating oils relatively soon after preparation.

#### EXAMPLE IV.

A dispersion of calcium nitrate in a lubricating oil containing a dispersant was prepared as follows. To a mixture of 1,000 ml of naphtha and 800 grams of a lubricating oil composition containing an overbased calcium sulfonate having an alkalinity value of about 290 (calcium content 11.4 percent w, about 4.13 equivalents of a basic reacting calcium compound was the overbasing material), in a three liter flask was added dropwise, with agitation, 335 grams of concentrated nitric acid (70%w HNO<sub>3</sub> = 3.72 equivalents of HNO<sub>3</sub>) over a 1 hour period. External cooling was not provided and the temperature rose from 74°F(23°C) to 104°F(40°C). Carbon dioxide and nitrogen oxides were evolved. After acid addition, the flask was fitted with a distillation apparatus and the temperature was raised to 280°F (138°C) to distill over the water and part of the naphtha solvent. The dehydrated mixture was filtered through Standard Supercell (a diatomaceous

earth filter aid available from Johns-Mansville). The naphtha solvent was then removed by the heating under vacuum to yield 843 grams of a clear, bright composition containing 27 percent w calcium nitrate. These concentrates were then compounded with lubricating oils and tested as shown in the following examples.

By the same procedure calcium nitrate was prepared dispersed in a lubricating oil containing carbonated, sulfurized calcium polypropylenephenate by adding nitric acid to a calcium overbased lubricating oil containing the dispersant. Prior to addition of the nitric acid, the overbased oil had an alkalinity value of about 260. By varying the quantity of acid added to the overbased oil, finished products containing calcium nitrate and having alkalinity values ranging from neutral up to about 100 were prepared.

#### EXAMPLE V.

Two series of test oils were prepared using a SAE50 oil as the base oil. The oils of both series contained sufficient amounts of an overbased calcium dispersant (calcium as the overbasing metal) to give the finished oil an alkalinity value of about 70. In addition the finished oils of both series contained sodium or calcium nitrate at the levels shown in Table V below. The dispersant in Series I was a carbonated calcium sulfonate and Series II was a carbonated, sulfurized calcium polypropylenephenate.

The oils were analyzed for sediment content (expressed as volume per cent of the total composition) using a test procedure similar to that described in ASTM method D2273. Briefly this method involves mixing 25 ml. of the test material with 75 ml of precipitation naphtha solvent by shaking well. The resulting mixture is then centrifuged at about 12,000 rpm for 15 minutes after which the sediment is rated. The results are shown in TABLE II.

In addition the antiwear properties of the oils were determined by means of the well known 4-ball test. In this test three ½ inch diameter steel balls are clamped together and immersed in the test lubricant. A fourth ball was then rotated at about 1,200 rpm in contact

with the other three balls. A 50 kg. load was applied for the time indicated and the temperature was maintained at 135°C. The sizes of the wear scars on the three stationary balls are measured and the average scar size in millimeters reported. In Table II below, the values reported are the average of three runs. The smaller the scar, the greater the antiwear properties of the lubricant. The 4-ball test is described in more detail in the *American Association of Lubrication Engineers Standard Handbook for Lubrication Engineers*, Chapter 27, James J. O'Connor, ed., McGraw-Hill, New York, 1968.

TABLE II.

4-BALL WEAR TESTS				
Nitrate Oil No.	cation	ppm <sup>(1)</sup>	Sediment % vol	4-ball wear scar, mm
				1 hr      2 hr
IA	None	—		0.449      0.473
IB	Na	540	0.08	0.438
IC	Na	2700	0.68	0.396
ID	Ca	540	Tr <sup>(2)</sup>	0.402
IE	Ca	2700	Tr	0.380
IIA	None	—	Tr	0.402
IIB	Na	540	0.05	0.407
IIC	Na	2700	0.07	0.398
IID	Ca	540	0.008	0.403
IIE	Ca	2700	Tr	0.403

<sup>(1)</sup> parts per million of nitrate

<sup>(2)</sup> Tr=trace

## EXAMPLE VI

A series of tests were run in a one cylinder high output diesel engine to determine the quantity of deposits which may form on the piston. The base oil used was a solvent refined neutral paraffinic oil having a viscosity of 480 SUS (Saybolt Universal Seconds) at 77°F. The engine is run for 16 hours with each sample of oil, disassembled, and visually rated for deposits. Each of the four ring grooves are rated on a scale from 0 to 100 with 0 representing no deposits and 100 representing heavy black deposits. Each of the three lands (the space between the ring grooves) are rated on a scale of from 0 to 800 with 0 representing no deposits and 800 representing heavy deposits. Deposits on the under-head of the piston, which is sprayed with crankcase oil for cooling purposes, are on a scale of from 0 to 10 with 10 representing no deposits. The results are shown in Table III below.

TABLE III.

Run No.	Base oil plus/kg of oil	Groove <sup>(1)</sup> Deposits	Land <sup>(1)</sup> Deposits	Under-head
1	50 mMols of sulfurized Ca polypropylenephenate AV=260	33-13-1.3-0.5	670-95-35	9.4
2	50 mMols of Ca sulfonate AV=290	44-4.6-1.3-0.5	360-80-45	9.1
3	50 mMols of Ca sulfonate-CaNO <sub>3</sub> as prepared in Ex. IV <sup>(2)</sup>	54-6.6-1.0-0.5	365-45-10	9.7
4	Same as Run No. 2	60-32-1.1-0.5	310-15-35	9.8

<sup>(1)</sup> In order from top of piston

<sup>(2)</sup> Equivalent to about 5000 ppm nitrate

The above data demonstrate that the quantity of deposits does not change significantly even when gross amounts of calcium nitrate plus a dispersant are incorporated into the crankcase oil, relative to overbased dispersants known to give acceptable deposit control.

## EXAMPLE VII.

Several test oils were prepared containing overbased calcium sulfonates and sulfurized calcium polypropylenephenates both with and without calcium nitrate as an antiwear agent. The base oil in each case was a high viscosity index oil to which was added sufficient overbased sulfonate or phenate and nitrate-dispersant (if used) to bring the total alkalinity value of the oil up to about 50.

These oils were used to lubricate the cylinder walls of a 3-cylinder Bolnes engine. The Bolnes three engine is a small (relatively speaking) marine propulsion diesel engine having two lubricating systems. One system lubricates the cylinder walls and the other the remainder of the engine. The cylinder walls are lubricated via a circumferential row of small ports in the wall itself. The flow of oil into the cylinder is regulated such that the amount of oil is sufficient to prevent scoring of the walls and to neutralize the acidic products of combustion. Most of the oil is burned during the combustion cycle but a small amount remains unburned to carry away ash and ash forming components of the oil. During the test runs, this drip oil was sampled periodically and analyzed for iron content which was taken as a measure of wear. Because most of the oil is burned during combustion the iron content of the drip oil is relatively high.

During each run with each test oil, the period from start up to 48 hours was taken as the break-in or stabilizing period for the test oil. Beginning with 48 hours the drip oil from each cylinder was sampled at 6 hour intervals and tested for iron content. Each test run was terminated at 72 hours. The iron content of the drip oil reported in Table IVA below is the average of the five values obtained from the five samples taken during the sample period.

TABLE IVA.

Run No.	1	2	3	4	5	6
Cylinder Oil <sup>(1)</sup> Wear, % w iron in drip oil <sup>(2)</sup>	1	2	2	1	3	4
Cylinder 1	83	87	95	70	75	66
Cylinder 2	90	53	57	97	89	67
Cylinder 3	103	26	32	71	92	66
Average	92	55	61	79	85	66

<sup>(1)</sup> See Table IVB for composition

<sup>(2)</sup> In one hundredths of one percent



TABLE IVB.

Cylinder Oil No.	Composition
1	Contains an overbased calcium sulfonate, AV of concentrate = 410
2	Same as 1 except contains 540 ppm nitrate as calcium nitrate prepared in Ex. IV.
3	Contains an overbased calcium polypropylene-phenate, AV of concentrate = 260
4	Same as 3 except contains 540 ppm nitrate as calcium nitrate prepared in Ex. IV.

As can be seen from the data in Table IVA, the presence of calcium nitrate in the cylinder oil in runs 2 and 3 markedly reduced wear (by an average of 32 percent) as compared with runs 1 and 4 which used the same oil without the nitrate. Similarly the presence of nitrate in run 6 reduced wear (by 22 percent) relative to run 5 which used the same oil without the nitrate.

EXAMPLE VIII.

This example demonstrates the desirability of incorporating additional oxidation inhibitors into oils containing the Group I and II metal nitrates. The results shown below in Table VA are those obtained from testing the oils in an oxidation test. This test measures the time required for the consumption of one (1) liter of oxygen by 100 grams of test oil at 340°F (170°C). In addition the total number of liters of oxygen consumed in 10 hours is determined as well as the percent viscosity (measured at 100°F(38°C)) increase for the 10 hour period.

Table VB shows the composition of the oils tested, the results of which are shown in Table VA.

TABLE VA.

OXIDATION TESTS				
Oil No.	Nitrate	Oxygen uptake		Viscosity Increase %
		Time to 1 liter, hr	Total uptake 10 hr, liters	
1A	No.	6.0	3.2	34
1B	Yes	6.0	4.5	67
2A	Yes	0.3	>13.8	1050
2B	Yes	2.8	6.6	128
2C	Yes	0.3	7.9	178
2D	Yes	6.5	5.6	65

TABLE VB.

OIL COMPOSITIONS	
Oil No.	Composition
1A	A commercially available railroad locomotive diesel engine lubricating oil, contains no calcium nitrate
1B	Same as 1A except contains 0.3 w% of calcium nitrate concentrate prepared in Ex. IV.
2A	Lubricating oil obtained from Casper, Wyo. oil fields; contains 3.54 w% of an oil solution of the reaction product of a succinic anhydride substituted with a polyisobutenyl radical having a number average molecular weight of 950 and tetraethylenepentamine approximately 44% active amide; and 80 mMols of Ca/kg of oil of the calcium nitrate-calcium sulfonate concentrate prepared in Ex. IV.
2B	Same as oil 2A plus 20 mMols of Zn/kg of zinc bis(polypropylenephenyl) dithiophosphate as an oxidation inhibitor
2C	Same as oil 2A except contains 75 mMols of Ca/kg of an overbased calcium sulfonate having AV = 275

TABLE VB.-Continued

OIL COMPOSITIONS	
Oil No.	Composition
2D	Same as oil 2C except contains 20 mMols of Zn/kg of the oxidation inhibitor of oil 2B

As can be seen from the data presented in Table VA, the presence of the calcium nitrate-calcium sulfonate dispersion increases the oxidative susceptibility and viscosity increase of the lubricating oils. However, it will be noted that the presence of small amounts of the oxidation inhibitor in oils 2B and 2D markedly reduced the oxygen uptake and viscosity increase relative to the oils without the oxidation inhibitor.

We claim:

1. A lubricating oil composition comprising:
  - a. An oil of lubricating viscosity, and
  - b. A nitrate of a Group I or Group II metal dispersed in said oil in an amount effective to substantially reduce wear.
2. The composition of claim 1 wherein said nitrate is dispersed in said oil with a dispersing agent selected from the group consisting of hydrocarbyl-substituted hydrocarbyl amines, hydrocarbyl-substituted hydrocarbyl amides, hydrocarbyl-substituted hydrocarbyl cyclicimides, metal sulfonates, metal phenates, hydrocarbyl-substituted metal carboxylates and mixtures thereof, wherein said metal is selected from the group consisting of Group I and Group II metals.
3. A lubricating oil composition of claim 2 wherein

the hydrocarbyl radical of said hydrocarbyl cyclicimides is an oil-solublizing polyolefin containing 12-200 carbon atoms and said cyclicimide is a succinimide.

4. A lubricating oil composition of claim 3 wherein said hydrocarbyl succinimide is a succinimide of a polyalkylene polyamine.

5. A lubricating oil composition of claim 4 wherein said hydrocarbyl succinimide is a polyisobutenyl succinimide of triethylene tetramine or a polyisobutenyl succinimide of tetraethylene pentamine.

6. A lubricating oil composition of claim 2, wherein said carboxylate dispersing agent is a naphthenate.

7. A lubricating oil composition of claim 6, wherein said Group I and Group II metals are selected from the group consisting of lithium, sodium, potassium, magnesium, calcium and barium.

8. A lubricating oil composition of claim 7, wherein said oil contains from 135 PPM to 50 percent weight of said nitrate of a Group I or Group II metal.

9. A lubricating oil composition of claim 8, wherein said dispersing agent is a sulfonate, phenate, or mixture

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thereof and said nitrate of a Group I or Group II metal is sodium nitrate.

10. A lubricating oil composition of claim 8, wherein said dispersing agent is a sulfonate, phenate or mixture thereof, and said nitrate of a Group I or Group II metal is calcium nitrate.

11. A lubricating oil composition of claim 7, wherein

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said oil contains from 180 to 3,000 PPM of said nitrate of a Group I or Group II metal.

12. A lubricating oil composition of claim 11, wherein said Group I and Group II metals are selected from the group consisting of lithium, sodium, potassium and calcium.

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