

Feb. 18, 1958

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2,824,068

ADDITIVE-CONTAINING OIL COMPOSITIONS AND THE LIKE

Filed Nov. 17, 1953

2 Sheets-Sheet 1

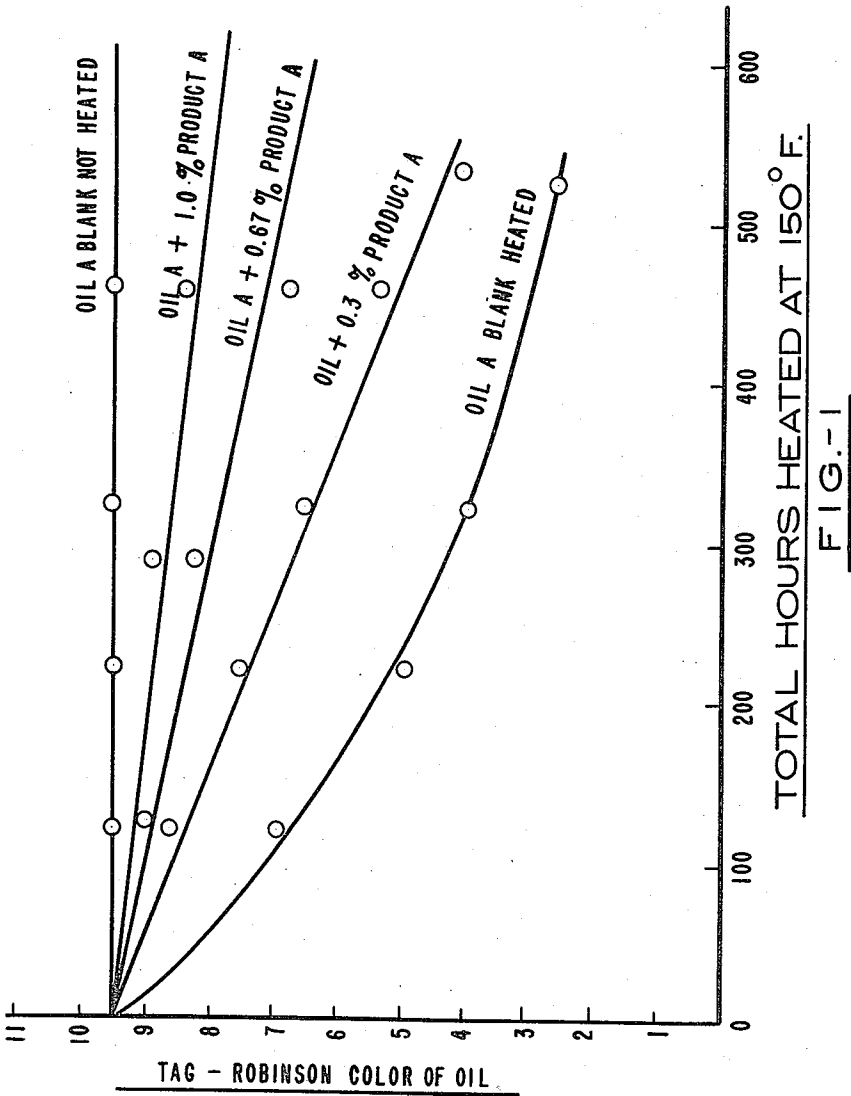


FIG.-1

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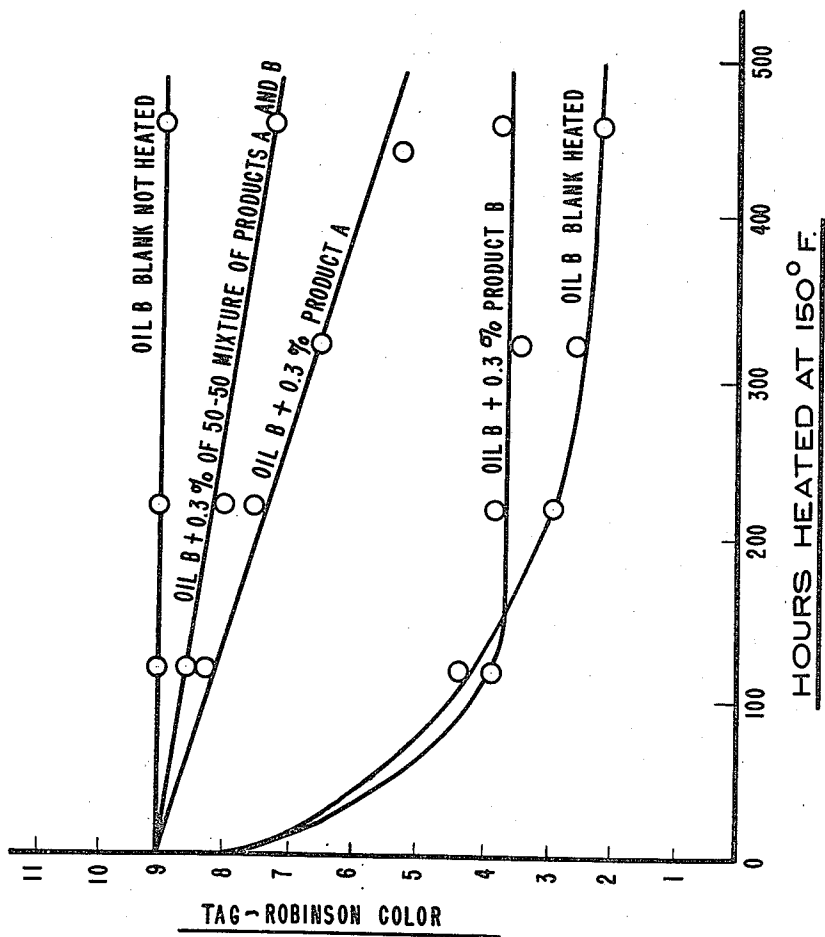


FIG. 2

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ADDITIVE-CONTAINING OIL COMPOSITIONS
AND THE LIKE

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Application November 17, 1953, Serial No. 392,644

9 Claims. (Cl. 252—49.9)

The present invention relates to the improvement of non-gaseous organic materials such as essentially hydrocarbon products, animal and vegetable fats and oils, and other natural and synthetic substances by the incorporation therein of a class of additives which impart improved properties to such compositions. The invention is particularly concerned with a class of compounds having utility as oxidation inhibitors, corrosion inhibitors, etc., when employed in relatively small concentrations in oleaginous materials such as lubricating oils and related substances.

In accordance with the present invention, it has been found that a special class of amine salts of phosphoric acids, when added to refined lubricating oils and the like in small proportions, substantially reduces the tendency of such oils to corrode surfaces. They are quite effective in inhibiting oxidation of petroleum hydrocarbon products, synthetic oils, and animal and vegetable oils that are susceptible to oxidation. The products of the present invention also have utility as rusting inhibitors. Since the products contain no metal, they are particularly useful as ashless additives in service where ash-forming constituents lead to harmful effects in engines operating under severe conditions.

The additives employed in the practice of the present invention may be broadly described as heterocyclic secondary amine salts of phosphoric acids in which one or more of the hydroxy groups in a phosphoric acid have added thereto a heterocyclic secondary amine which has a sufficiently high basicity to form a salt. In a preferred embodiment, the amine radical in these salts contains no unsaturation adjacent the heterocyclic nitrogen atom; the completely saturated heterocyclic secondary amines are particularly useful. These compounds have been found to have outstanding properties as anti-oxidants for organic materials susceptible to oxidation, showing unexpected superiority in this respect over various other types of amine salts, such as acyclic amine phosphates.

In a preferred modification of the present invention, a combination of the foregoing described heterocyclic amine phosphates and of an acyclic secondary amine salt of a phosphoric acid is employed as an additive composition. It has been found that this combination imparts unexpectedly improved properties to the composition to which it has been added, in this respect showing a synergistic improvement over the performance obtained from either type of amine phosphate when used alone. The specific types of amine phosphates and the relative proportions of the two types of phosphates used in this combination will be discussed in more detail hereinafter.

Although the above described compounds impart a number of useful properties to materials of the type described above, they have been found to be particularly useful in inhibiting oxidation, especially in preventing color degradation, of oily materials during processing, transportation or storage. Although it is not desired

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to be bound by theoretical considerations, it is believed that the effectiveness of these compounds as anti-oxidants depends upon a buffer action which reduces the acidity of the material, and also to the formation of complexes with metals when the oily material contacts metal parts that have a catalytic action in causing oxidation.

In the drawings:

Figure 1 presents a family of curves showing the relation between colorhold of oil, with and without secondary heterocyclic amine phosphate, versus heating time;

Figure 2 presents a comparison of the effect of heterocyclic and acyclic secondary amine phosphates and their mixtures on the stability of oil.

The preparation and testing of compounds of the present invention are illustrated by the examples to be described in detail below, but such examples are not to be construed as limiting the scope of the invention in any manner.

EXAMPLE 1.—PREPARATION OF PRODUCTS

Product A.—Preparation of piperidine phosphate

To 100 grams (1.2 mol) of piperidine, 200 ml. of isopropyl alcohol were added. The mixture was cooled to 10° C. in an ice-salt bath, then a solution of 43 grams of 90% phosphoric acid (0.4 mol) in 80 ml. of isopropyl alcohol was added slowly. The maximum temperature was 25° C. The solution contained the product as a heavy suspension of white crystals. The soluble portion was removed by adding 220 ml. of isopropyl alcohol, heating to boiling, and then filtering. The residue was washed with 200 ml. of hot isopropyl alcohol and dried in a stream of air. The resulting product contained 16.5% phosphorus, 6.72% nitrogen and consisted chiefly of mono-piperidine phosphate.

Product B.—Preparation of di-octadecyl amine phosphate

To 20 grams (0.04 mol) of di-octadecyl amine, 1.4 grams of 90% phosphoric acid (0.013 mol) was added, followed by 40 ml. of isopropyl alcohol. The mixture was heated, giving a deep yellow solution. On cooling, crystals formed. The mixture was filtered and the residue washed with isopropyl alcohol and hexane. The product was dried in air to give a soft, white solid material containing 2.19% phosphorus and 2.37% nitrogen.

EXAMPLE 2.—TESTING PRODUCTS AS ANTI-
OXIDANT ADDITIVES

The products described in Example 1 were tested as mineral lubricating oil anti-oxidants by the following procedure. A blend of the product dissolved in a mineral oil base stock, to be described specifically below, was exposed to cyclic conditions of heating and cooling. To do this, 300 g. of the oil blend were put in a 600 cc. Pyrex glass beaker, and a sand-blasted steel panel was supported in the beaker so that $\frac{3}{4}$ of the panel was covered by the oil. The oil blends were heated at 150° F. for about 100 hours, then cooled to room temperature, examined for color and then heated again for another period of 100 hours. This heating and cooling was continued until the samples had been exposed to the elevated temperature of 150° F. for a total of from 500 to 600 hours. In each case, the Tag-Robinson color of the oil blend was determined before subjecting to the heating test and after each period of heating. The steel panels were also examined for evidences of rust.

The oils used in these experiments, designated as oils A and B, were Venezuelan distillates, each having an S. U. S. viscosity at 210° F. of about 55. In one series of tests, portions of oil A were blended with 0.3 weight percent, 0.67 weight percent, and 1.0 weight percent of product A. Each of these blends and a sample of the

unblended oil were tested by the above procedure. The results of these tests are shown in Figure 2, presenting a family of curves of the Tag-Robinson color of the oil vs. the number of hours that the oils were heated at a temperature of 150° F. It is noted that oil A without the additive lost color rather rapidly, and at the end of 500 hours had a color of about 3 Tag-Robinson units. The oils containing product A showed excellent color stability characteristics, the blend containing 1% of product A losing less than 1½ color units after about 500 to 600 hours.

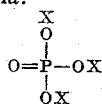
In another series of tests, oil B without additives and blends of oil B containing 0.3 weight percent product A, or 0.3 weight percent product B, or 0.3 weight percent of a mixture containing equal parts of products A and B, were each tested by the above described procedure. The results of these tests are shown in Figure II, presenting a family of curves of color vs. hours heated at 150° F. It is noted that product B gave little or no improvement to the oil during the first 200 hours heating and only a slight improvement over the uninhibited oil during the remaining portion of the heating period. Product A imparted a substantial improvement to the oil in contrast to product B; however, the combination of products A and B, at a concentration level corresponding to that used in the case of either of the products alone, resulted in an oil blend that was almost completely stabilized. It would normally be expected that a 50/50 mixture of products A and B at this concentration level would give a color-hold of only about 4½ units at 500 hours whereas a color-hold of about 7½ units at 500 hours was actually obtained. This represents a substantial and unexpected improvement.

It is also interesting to compare the results shown in Figures 1 and 2, since the oil base stocks A and B were substantially the same. It is noted that the combination of products A and B at an 0.3 weight percent level gave results substantially equivalent to that obtained with 1.0 weight percent of product A alone.

Other runs made with product B in such mineral oil base stocks showed consistently that this acyclic amine phosphate, at concentration levels of up to as high as 1% by weight, imparted no substantial improvement to the oil up to heating times as high as about 400 hours, and that the improvement obtained thereafter was consistently less than that obtained with the heterocyclic amine phosphate.

It was also significant that the steel panels used in the color-hold tests were consistently rusted or corroded by the uninhibited oil base stocks, but that no corrosion was recorded after 500 to 600 hours heating by the inhibiting oils, particularly with those containing product A alone or in combination with product B.

The heterocyclic amine salts employed in the practice of the present invention are preferably those represented by the following formula:

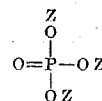


wherein X is selected from the class consisting of hydrogen and heterocyclic secondary amine radicals, at least one X being a heterocyclic amine radical. Because of steric hindrance and other considerations, it is usually difficult to prepare such compounds in which all of the hydroxyl groups have reacted with amine radicals. The heterocyclic amine radicals preferably contain in the range of from 5 to 24 carbon atoms, and as mentioned before do not contain any unsaturation adjacent the nitrogen atom in the ring. Completely saturated heterocyclic rings are preferred. These salts are readily prepared by prior art procedures such as by merely reacting together a phosphoric acid and the desired amine, preferably in the presence of a solvent. Such processes are well known to the art and will not be described in detail herein.

Phosphoric acid is the preferred acid to be used in the preparation of these compounds, although various polyphosphoric acids or oxides of phosphorus that will form phosphates may be employed.

The heterocyclic amines to be employed in forming the phosphates are those having a relatively high basicity sufficient to react with the phosphoric acid. Suitable basic compounds include piperidine; 1-ethylpiperidine; 3-ethylpiperidine; 1-amyloxy; 1,2-dimethylpiperidine; 1-dodecylpiperidine; 1-nonylpiperidine; and other derivatives of piperidine containing one or more alkyl, alkenyl, cycloalkyl, arylalkyl and the like substituent groups. The partially and completely hydrogenated quinoline derivatives are also useful, such as 2-methyldecahydroquinoline; dihydroquinoline; tetrahydroquinoline; decahydroquinoline; tetrahydroquinoline; and other hydrocarbon substituted derivatives of these types of compounds. The partially and completely hydrogenated acridine compounds such as tetrahydroacridine, dodecylhydroacridine and the like are suitable.

When it is desired to employ a secondary acyclic amine salt in combination with the above described heterocyclic amine phosphates, the preferred compounds are those having the following general formula:



wherein Z is selected from the group consisting of hydrogen and acyclic secondary amine radicals, and at least one Z is an amine radical. It is preferred that each acyclic hydrocarbon group in the amine radical contain in the range of 10 to 30 carbon atoms, preferably 12 to 24 carbon atoms. The acyclic hydrocarbon portion of the amines include alkyl, alkenyl and the like radicals although the saturated hydrocarbon radicals are preferred. Such amines are readily prepared by reacting a desired phosphoric acid or oxide of phosphorus with the amine as heretofore discussed in connection with the preparation of the secondary heterocyclic amine phosphates.

Specific secondary acyclic amines useful in the reaction to prepare the phosphates include didecylamine, didodecylamine, dicetylamine, dioctadecylamine, dioctadecylamine, and other such higher amines which may be derived from animal fats and oils, secondary wax amines such as the di-C₂₀ to C₂₄ wax amines, and the like.

In choosing a secondary heterocyclic amine salt to be used in the practice of the present invention, consideration should be given to the type of base stock to which it is added and the specific property to be improved. Obviously, solubility factors will limit to some extent the specific type of salt to be employed. The lower molecular weight salts having relatively small oil solubilizing groups are less preferred than corresponding high molecular weight members when the salts are to be used in relatively high concentrations in mineral lubricating oils and the like. In general, in the range of about 0.01 to 5.0% by weight of the amine salt, based on the total composition, will be satisfactory for inhibiting oxidation, corrosion or rusting of metal parts. Generally, the range of 0.1 to 2.0 weight percent will be most effective for antioxidant properties. Amounts in the range of 5 to 15% or even higher may be used for imparting these and other desirable characteristics to mineral lubricating oils and the like. For convenience in transporting and storing the nitrogen base salts, it is frequently desirable to prepare concentrates containing in the range of about 20 to 50% by weight of the salt in a mineral oil base stock such as a lubricating oil, and then adding a desired amount of the concentrate to the base stock to be improved in preparing the final blend. In general, compositions prepared in accordance with the present invention will include a major proportion of the oil base stock and minor proportions of the nitrogen base salts. The oil

compositions may, of course, include minor amounts of other additive materials as will be described below.

When it is desired to employ the combination of one or more of the foregoing heterocyclic amine phosphates with an acyclic amine phosphate, the two compounds may be mixed in a weight ratio ranging from about 0.1 to 10 parts of the acyclic amine salt per part of heterocyclic amine salt with a preferred ratio being about 0.3 to 3.0 parts per part, respectively. Although these combined additives may be used in somewhat smaller concentrations as inhibitors and the like than is required for accomplishing the same potency with the heterocyclic type alone, the general concentration ranges given above apply as well for the combination additive.

The products of the present invention may be employed not only in ordinary lubricating oils but also in the "heavy duty" type of lubricating oils which have been compounded with such detergent type additives as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal organo phosphates, thiophosphates, phosphites and thiophosphites, metal salicylates, metal xanthates and thioxanthates, metal thiocarbamates, amines and amine derivatives, reaction products of metal phenates and sulfur, reaction products of metal phenates and phosphorus sulfides, metal phenol sulfonates, and the like. Thus, the additives of the present invention may be used in lubricating oils containing such other addition agents as barium tert.-octylphenol sulfide, calcium tert.-amylphenol sulfide, nickel oleate, barium stearate, calcium phenyl stearate, zinc diisopropyl salicylate, aluminum naphthenate, calcium cetyl phosphate, barium di-tert.-amylphenol sulfide, calcium petroleum sulfonate, zinc methylcyclohexyl thiophosphate, calcium dichlorostearate, etc. Other types of additives such as phenols and phenol sulfides may be employed.

The lubricating oil base stocks used in the preferred compositions of this invention include animal, vegetable, mineral and synthetic oils. Preferably, they are essentially hydrocarbon oils such as straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, furfural, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins; e. g., high molecular weight polyisobutylenes, or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coal tar fractions and coal tar or shale oil distillates may also be used. Also, for special application, animal, vegetable or fish oils or their hydrogenated or volatized products may be employed alone or in admixture with mineral oils. Synthetic oils of the ester, polyester, polyether and related types may also be used. These include di-2-ethylhexyl sebacate, dibasic acid esters, polyalkylene oxides, etc.

For the best results, the base stock chosen should normally be that oil which without the new additive present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must, of course, be observed. The oils must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. Lubricating oils, however they may have been produced, may

vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 35 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed diesel engines, the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of diesel engines, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index.

In addition to the material to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like may also be employed. Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol ($C_8H_{17}OH$), lauryl alcohol ($C_{12}H_{25}OH$), cetyl alcohol ($C_{16}H_{33}OH$), stearyl alcohol, sometimes referred to as octadecyl alcohol ($C_{18}H_{37}OH$), heptadecyl alcohol ($C_{17}H_{35}OH$), and the like.

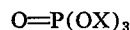
In addition to being employed in crankcase lubricants, the additives of the present invention may also be used in extreme pressure lubricants, engine flushing oils, industrial oils, general machinery oils, refrigeration oils, process oils, rust preventive compositions and greases.

The additives of the present invention may be used in lubricants of the types described above and also in other organic materials including petroleum hydrocarbon products generally, where improved resistance to oxidation or other improved properties are desired. Thus, the products may be added to motor oils, diesel fuels, kerosene, waxes, hydrocarbon polymers, etc., and other mineral oils. The agents may also be added to natural and synthetic rubbers, asphalts, plastics and other solid and liquid organic materials.

The present invention is not to be considered as limited by any of the examples described herein, which are given by way of illustration only, but is to be limited solely by the terms of the appended claims.

What is claimed is:

1. A lubricating composition comprising a major proportion of an essentially hydrocarbon oil and about 0.01 to 20% by weight, based on the total composition, of a saturated heterocyclic secondary amine phosphate containing about 5 to 24 carbon atoms and having the formula:



wherein X is selected from the group consisting of hydrogen, amine radicals of piperidine and amine radicals of alkyl substituted piperidine, at least one X being an amine radical.

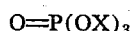
2. A lubricating composition comprising a major proportion of an essentially hydrocarbon oil and about 0.01 to 20% by weight based on the total composition, of piperidine phosphate.

3. A lubricating oil composition consisting essentially of a mineral lubricating oil and in the range of 0.1 to 5% by weight of piperidine phosphate.

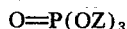
4. A lubricating composition comprising a major proportion of a mineral oil and about 0.01 to 20% by weight, based on the total composition, of a mixture consisting essentially of a saturated heterocyclic secondary amine

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salt of phosphoric acid containing about 5 to 24 carbon atoms and having the formula:

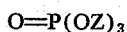


wherein X is selected from the group consisting of hydrogen, amine radicals of piperidine and amine radicals of alkyl substituted piperidine, at least one X being an amine radical; and an acyclic secondary amine salt of a phosphoric acid containing about 10 to 30 carbon atoms and having the formula:



wherein Z is selected from the group consisting of hydrogen and acyclic secondary amine radicals, at least one Z being an amine radical; the weight ratio of said salts being in the range of about 0.1 to 10 parts of said acyclic amine salt per part of heterocyclic amine salt.

5. A lubricating composition comprising a major proportion of a mineral oil and about 0.01 to 20% by weight, based on the total composition, of a mixture consisting essentially of a piperidine phosphate and an acyclic secondary amine salt of phosphoric acid containing about 10 to 30 carbon atoms and having the formula:



wherein Z is selected from the group consisting of hydrogen and acyclic secondary amine radicals, at least one Z being an amine radical; the weight ratio of said salts being in the range of about 0.1 to 10 parts of said acyclic amine salt per part of piperidine phosphate.

6. A composition as in claim 5 wherein said acyclic amine salt is didodecyl amine phosphate.

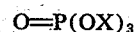
7. A composition as in claim 6 wherein said mixture

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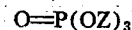
includes substantially equal proportions of said heterocyclic amine phosphate and acyclic amine phosphate.

8. A composition as in claim 7 consisting essentially of a mineral lubricating oil and in the range of 0.1 to 5% by weight of said mixture.

9. A mineral oil concentrate consisting essentially of mineral lubricating oil and 20 to 50 weight percent of a mixture of a heterocyclic secondary amine salt of a phosphoric acid having the formula:



wherein X is selected from the group consisting of hydrogen, amine radicals of piperidine and amine radicals of alkyl substituted piperidine, at least one X being an amine radical; and an acyclic secondary amine salt of phosphoric acid having the formula:



wherein Z is selected from the group consisting of hydrogen and acyclic secondary amine radicals, at least one Z being an amine radical, said salts being present in the range of about 0.1 to 10 parts of said acyclic amine salt per part of said heterocyclic amine salt.

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