Patented Mar. 27, 1945 2,372,588

UNITED STATES PATENT OFFICE

2,372,588

COMPOUNDED MINERAL OIL

Robert G. Larsen, Berkeley, and Ernest W. Zublin, San Francisco, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application June 19, 1940, Serial No. 341,308

13 Claims. (Cl. 252—39)

This invention relates to compounded mineral oils, and more particularly deals with relatively high-boiling oils, such as lubricating oils, electrical oils, insect spray oils containing oil-soluble compounds of derivatives of pyridine, its homologues and analogues. Oils to which this invention is particularly applicable, though not necessarily limited, are those which, during their useful lives, are not, or not completely, vaporized or burned.

It is known that the addition of certain salts of carboxylic acids, sulfonic acids, etc., to mineral lubricating oils has beneficial effects in many respects. Thus, it is known that the ring-sticking tendencies of Diesel engines or aviation engines may be retarded or prevented by the addition of such salts to oils with which they are lubricated. Moreover, lubricating oils may be improved with regard to sludge-forming tendencies, viscosity index, pour point, oiliness, etc., by the addition of such salts.

It is a purpose of this invention to produce mineral oils having their properties improved in one or several respects by adding thereto metal derivatives of heterocyclic aromatic compounds containing nitrogen in the aromatic nucleus. It is another purpose to provide anti-ringsticking lubricants. Another purpose is to prevent or retard sludging of lubricants, electrical oils, etc., during their use. Still another purpose is to provide a new class of fungicidal and insecticidal spray oils. A futher purpose is to provide a class of oil-soluble addition compounds for mineral oils which are more effective in many respects, and in some ways have entirely new properties as compared with similar compounds heretofore suggested.

We have discovered that a new class of metal compounds wherein a metal is linked through a metal-active radical containing metal and replaceable hydrogen to an aromatic heterocyclic nucleus consisting of nitrogen and carbon, at least one nuclear nitrogen being trivalent, have especially useful properties when blended with mineral lubricating oils in relatively small quantities. One of the most outstanding properties of these compounds is their ability to dissolve and finely disperse sludge, which thereby is rendered harmless due to its being prevented from settling or accumulating on surfaces in need of lubrication. In this property our compounds are far more efficient than the corresponding compounds based on carbocyclic rings. Moreover, the basic reacting nuclear nitrogen effects a considerable reduction in the harmful effect of corrosive free acids which are often formed by oxidation during the useful life of many of the oils.

The compounds of our invention may be divided into two general classes, namely, salts and amides. In the salt a metal and an acid derivative of a pyridine or its homolgues or analogues are combined, while in the amide the metal substitutes one or several hydrogen atoms in an amino radical of an amino pyridine or its homologues or analogues.

For the purpose of this invention, we define homologues of pyridine, quinoline, etc., as those derivatives in which one or several replaceable hydrogen atoms of the aromatic nucleus are substituted with radicals, such as hydrocarbon, hydroxy, carboxy, ether, hydrosulfide, sulfide, amino, imino, halogen, nitro, nitroso, nitrile, sulfonic, etc., radicals. Analogues, on the other hand, are those compounds which contain different numbers of nitrogen in the nucleus, or whose nuclei contain different numbers of condensed aromatic rings, or the same number differently arranged. Thus, chlorpyridine is a homologue of pyridine, while quinoline or pyrimidine are analogues of pyridine.

The metal amides of our invention are in general good sludge suppressors, many of them acting as anti-oxidants while others function primarily as sludge dispersers. If they contain hydrocarbon radicals of relatively high molecular weights, they may be effective as pour point depressors, viscosity index improvers, anti-corrosion agents, etc.

The salts are useful as sludge dispersers, anti-ringsticking compounds, oxidation retarders, anti-lacquering agents, pour point depressors, viscosity index improvers, etc. All these properties will, of course, vary with the configuration of the organic radicals, the types of substitution radicals and the metal employed, one or more effects being predominant, while one or more of those enumerated above may be completely absent.

Most useful in lubricating oils are in general salts, the organic portions of which contain at least one relatively long carbon chain having 10 or more carbon atoms. These salts are effective detergents for anti-ringsticking properties. If their molecular weights are relatively high, e. g., above about 800, they also improve the V. I.

It is known that the addition of various oil-soluble metal compounds, such as salts of fatty acids, naphthenic acids, aromatic fatty acids, alkyl benzoic acids, petroleum sulfonic acids, etc., render lubricating oils corrosive. Thus the presence in lubricating oils of salts which combine certain metals with certain of the acids causes corrosiveness of the freshly blended oil, which corrosiveness is aggravated as the oil is used in internal combustion engines. Salts of other metals, particularly when combined with acids of very high molecular weights, may result in oils which, when fresh and unused, are non-

corrosive or may even be anti-corrosive toward the same bearing metals. However, upon use as crank case oils in internal combustion engines, these originally non-corrosive oils also become corrosive.

The reason for the corrosiveness of the oils containing these salts is not clear, especially when the salts are substantially neutral or basic. Moreover, the rapid increase in the corrosiveness upon use of the oil is difficult to explain.

Whatever the reason for the observed corrosiveness may be, we have discovered that the salts of our acids are considerably less corrosive than the salts of the corresponding acids based on carbocyclic compounds, and if they are corrosive, the corrosiveness of the former is much more completely and more lastingly inhibited than that of the latter by the addition of oxidation inhibitors.

As previously stated, the metal may be bound to the pyridine or its homologues or analogues, through a metal-active amino or acid radical or both. If an amino radical provides the only bond for the metal, then this radical must in its free state possess at least one replaceable hydrogen atom. Thus primary and secondary amino radicals may be suitable. Suitable acid radicals are, for instance, —OH, —SH, —COOH, —CSOH, —SO_2OH. These metal-active radicals may be attached directly to the aromatic nuclei or may be linked thereto through a bridge of one or several carbon atoms, which bridge may contain ether, thioether, imino ether, etc., linkages.

Particularly valuable metal compounds are obtained if the non-metallic portion contains two or more metal-active radicals, i. e., amino or acid radicals or both. Thus a combination of an amino and an acid radical, or of an —OH or —SH and a carboxyl radical are particularly desirable, especially if the metal-active radicals happen to be separated from each other by a bridge of 3 to 4 carbon atoms. This bridge may, if desired, contain ether, thioether or imino ether links. The metal-active radicals may be attached to the same or to different aromatic nuclei, at least one of which contains a nuclear nitrogen, and which are in close proximity to each other.

The position of the metal-active radical relative to the nuclear nitrogen atom may also be of some importance. In general, more stable metal compounds are obtained if this radical is separated from the ring nitrogen by two or three carbon atoms.

In order to exert their beneficial effect, the metal compounds must be soluble in hydrocarbon oils in effective quantities, and this may in most instances require the presence of oil-solubilizing groups, such as one or several alkyl, naphthenyl, aryl or aralkyl, etc., radicals. Such radicals may be introduced into the aromatic nucleus, for example, by reacting suitable chlorinated hydrocarbons, such as chlorinated kerosene, gas oils, lubricating oils, extracts or raffinates thereof, wax, or of pure hydrocarbons, such as butanes, pentanes, hexanes, octanes, dodecanes, cetanes, etc., or corresponding alcohols or olefines, with the pyridine compounds, its homologues or analogues, in the presence of a suitable condensing catalyst such as a Friedel-Crafts catalyst, sulfuric acid, phosphoric acid, P_2O_5, etc. The products of this reaction comprise derivatives of pyridine, or its analogues, wherein at least one hydrogen of the nucleus has been replaced by the hydrocarbon radical. The solubilizing radicals may themselves, if desired, contain substitution radicals, such as halogen, hydroxy, ether, hydrosulfide, thioether, amino, imino, etc., radicals. Moreover, they may be connected to the pyridine or homologous nucleus through an ether, thioether or imino ether linkage.

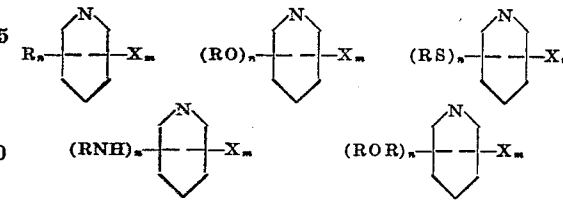
Further, the pyridine or analogous nucleus may, in addition to the acid or amino radical, contain other substitution radicals, such as halogen, nitro, nitroso, nitrile groups.

The active radical or radicals which links the metal to the pyridine compound or its analogue may be introduced by various known reactions. For example, SO_3H radicals may be introduced by simple sulfonation. Sulfonated compounds so produced may in turn be treated with alkalis at high temperatures to convert them to the corresponding hydroxy compounds. Amino derivatives may be obtained by treating chlorinated pyridine or analogue with ammonia. Likewise, thiopyridines may be produced by treating chlorinated pyridines with KSH. Pyridine carboxylic acids may be made by oxidation of alkyl pyridines with $KMnO_4$, etc.

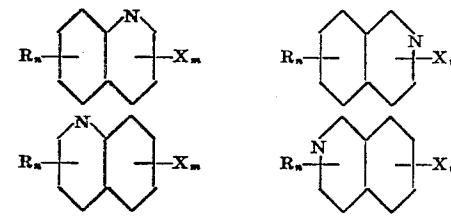
In producing our compounds, we may start out with substantially pure pyridines, quinolines, etc., or we may use mixtures of different analogues, such as mixtures of quinoline and isoquinoline, or pyridine and quinoline, or alkylated pyridines, quinolines, isoquinolines, etc. A suitable source for the production of such mixtures are cracked hydrocarbon oils, such as cracked naphthas, kerosenes, gas oils, etc.

In the table below, a series of formulae of pyridine derivatives and analogues of pyridine are listed which are suitable for producing our oil-soluble salts. In these formulae, R represents a hydrocarbon radical which may contain substitution groups; n and m are integers, the sum of which is not greater than the number of replaceable hydrogens in the pyridine or analogous nuclei; X is an acidic or amino radical.

Pyridines

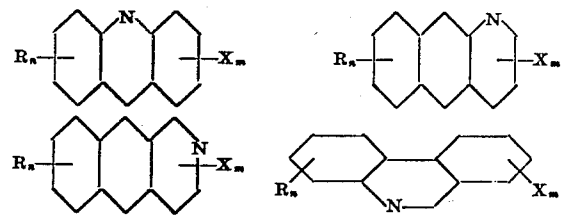


Quinolines and isoquinolines



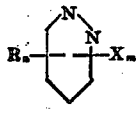
ethers, thioethers, imino ethers, etc., equivalent to those of the pyridines.

Acridines, anthrapyridines, phenanthridines

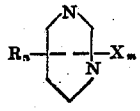


Derivatives equivalent to those shown above.

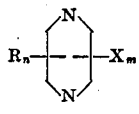
Diazines



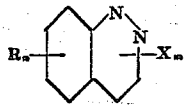
Pyridazine



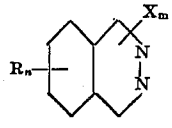
Pyrimidine



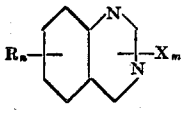
Pyrazin



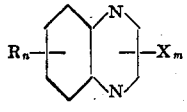
Cinnoline



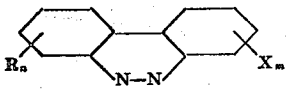
Phthalazin



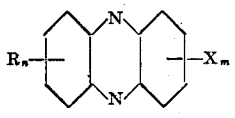
Quinazoline



Quinoxaline

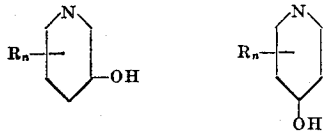


Phenazone

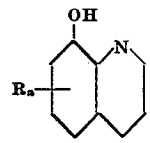


Phenazine

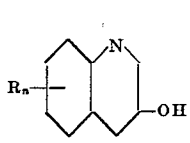
Below are listed some compounds, the salts of which are preferred for our purpose:



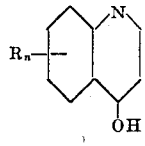
Alkyl 3- and 4-hydroxy pyridines



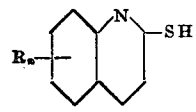
Alkyl 8-hydroxy quinoline



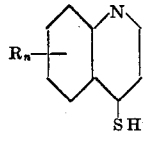
Alkyl 3-hydroxy quinoline



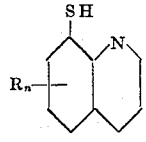
Alkyl 4-hydroxy quinoline



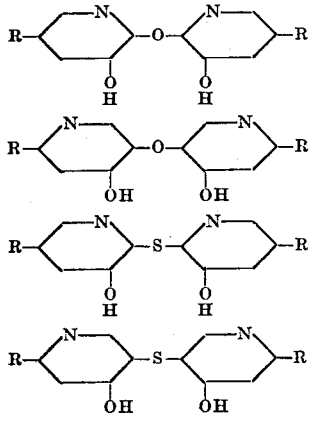
Alkyl 2-thio quinoline



Alkyl 4-thio quinoline

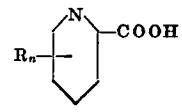


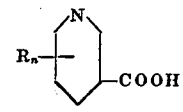
Alkyl 8-thio quinoline

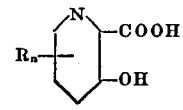


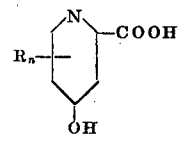
hydroxy pyridyl ethers, thioethers and corresponding imino ethers.

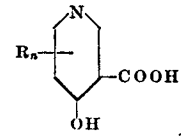
Carboxylic acids

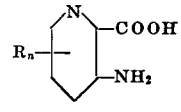


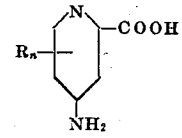


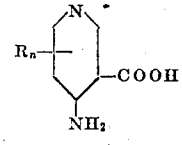


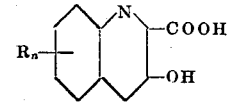


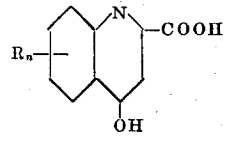


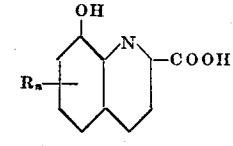


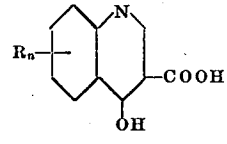






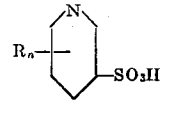


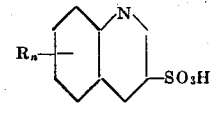




etc.

Sulfonic acids





etc.

Mixtures of metal derivatives of the above compounds may be used if desired. Furthermore, in addition to our compounds, we may also incorporate in lubricating or other mineral oils conventional anti-oxidants, pour point depressors, corrosion inhibitors, extreme pressure agents, blooming agents, dyes, etc.

Depending upon the particular type of improvement which is to be achieved by the metal compounds of our invention, different metals may be combined with the amino or acid radicals of our compounds. Thus we may incorporate in the mineral oils salts of the alkali metals, i. e., lithium, sodium, potassium; alkali earth metals, i. e., Mg, Ca, Sr, Ba; earth metals, i. e., Al, Tl; heavy metals, i. e., Cu, Ag, Zn, Cd, Hg, Sn, Pb, As, Sb, Bi, Cr, Mo, W, Mn, Fe, Ni, Co, etc. In lubricating oils we usually prefer the compounds of the polyvalent light metals, i. e., Mg, Ca, Sr, Ba, Al. Compounds of metal which are toxic to the lower forms of life, e. g., of Pb, Ag, As, Sb, Tl, etc., and particularly Cu, are very valuable in insecticidal and fungicidal oils.

In many instances, we also may employ salts of relatively strongly basic amines such as quaternary ammonium bases, i. e., tetramethyl, tetra-

methyl ethyl, dimethyl diethyl, trimethyl benzyl, dimethyl ethyl benzyl, methyl triisopropyl, triisopropyl benzyl ammonium bases; or piperidine, guanidine, etc. Very useful are salts of these strong basic amino compounds with sulfonic acids of pyridine, its analogues and homologues.

The amounts of our compounds to be incorporated in mineral oils may vary depending upon the effect desired. In general, quantities ranging from about .1% to 10% are useful.

We claim as our invention:

1. A sludge retarding mineral oil composition containing dissolved a small mount of an oil-soluble metal salt of a monocarboxylic acid of a heterocyclic aromatic compound, the aromatic six-membered nucleus of which consists of carbon and nitrogen, at least one nitrogen being trivalent.

2. The composition of claim 1 wherein the amount of the metal derivative is from .1%–10%.

3. A sludge retarding mineral oil composition containing dissolved a small amount of an oil-soluble metal salt of a monocarboxylic acid of a heterocyclic aromatic compound, the aromatic six-membered nucleus of which consists of carbon and nitrogen, at least one nitrogen being trivalent, said aromatic compound having at least one replaceable nuclear hydrogen substituted by an oil-solubilizing radical.

4. The composition of claim 3 wherein said solubilizing radical is an aliphatic radical of at least 10 carbon atoms.

5. A sludge retarding mineral oil composition containing dissolved a small amount of an oil-soluble metal salt of a monocarboxylic acid of pyridine.

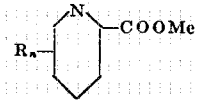
6. A sludge retarding mineral oil composition containing dissolved a small amount of an oil-soluble metal salt of a monocarboxylic acid of quinoline.

7. A sludge retarding mineral oil composition containing dissolved a small amount of an oil-soluble salt of a monocarboxylic acid of a heterocyclic aromatic compound, the aromatic six-membered nucleus of which consists of carbon and nitrogen, at least one nitrogen being trivalent, said metal being linked to the aromatic compound through an active radical, which in its free state contains metal-replaceable hydrogen, said active radical and nuclear nitrogen atom being separated from each other by 2 or 3 carbon atoms.

8. A sludge retarding mineral oil composition containing dissolved a small amount of an oil-soluble metal salt of a monocarboxylic acid of an aromatic compound comprising not less than one heterocyclic aromatic six-membered nucleus which consists of carbon and nitrogen, at least one nitrogen being trivalent, said compound containing at least two metal-active radicals separated from each other by a bridge of 3 to 4 carbon atoms.

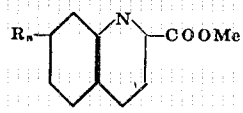
9. The composition of claim 8 wherein said bridge contains a linkage selected from the group consisting of ethers, thioethers and imino ether linkages.

10. A sludge retarding mineral oil composition containing a small amount of an oil-soluble heterocyclic aromatic metal compound having the formula



wherein R is an oil-solubilizing radical, Me is a metal equivalent of hydrogen and n is an integer which is not greater than the number of replaceable hydrogens of the aromatic nucleus.

11. An improved mineral oil composition containing dissolved an oxidation-inhibiting amount of an oil-soluble metal carboxylate having the formula



wherein R is selected from the group consisting of hydrogen atoms, hydrocarbon and substituted hydrocarbon radicals, Me is a metal equivalent of hydrogen and n is an integer which is not greater than the number of replaceable hydrogens of the quinoline nucleus.

12. The composition of claim 11 wherein Me is calcium.

13. The composition of claim 6 wherein the metal is an alkali earth metal.

ROBERT G. LARSEN.
ERNEST W. ZUBLIN.