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3,740,338

GUANIDINIUM SALTS AND FUNCTIONAL FLUIDS CONTAINING THEM

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No Drawing. Continuation-in-part of abandoned application Ser. No. 17,913, Mar. 3, 1970. This application June 7, 1971, Ser. No. 150,759

Int. Cl. C09k 3/00

U.S. Cl. 252—77 7 Claims

ABSTRACT OF THE DISCLOSURE

Phenoxide and naphthoxide salts of guanidine and hydrocarbon substituted guanidine are disclosed. Also disclosed are automatic transmission fluids and other functional fluids containing these salts as base reserve additives and anti-oxidants.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 17,913, filed Mar. 3, 1970 and now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to automatic transmission fluids and other functional fluids containing guanidine compounds as ashless basic additives.

The term "functional fluids," as herein used, includes those hydrocarbon fluids whose principal function is to transmit force, and which serve only incidentally as lubricants. Such fluids include automatic transmission fluids, hydraulic fluids, and the like, but do not include vehicular and industrial fluid lubricants such as motor oil or gear oil. The functional fluids, and particularly the automatic transmission fluids, commonly contain a number of additives such as anti-wear agents and viscosity index improvers. They often also contain base reserve additives whose function is to neutralize acids which are formed in the fluid during operation in transmissions or hydraulic equipment. These base reserve additives are commonly basic salts of alkali or alkaline earth metals.

Functional fluids also often contain anti-oxidant additives. These serve to inhibit the occurrence of oxidation when the fluid is subjected to elevated operating temperatures in the presence of an oxygen source such as air. Oxidation of the fluid is often marked by an undesirable increase in its viscosity.

Description of the prior art

U.S. Pat. 1,830,970 discloses use of the higher fatty acid soaps of guanidine and guanyl derivatives in lubricating oils and standard transmission gear oils. These additives are present in the oil as 0.2 to 0.5 weight percent and are said to increase the lubricating properties of the oil. U.S. Pat. 2,401,733 discloses use of guanidinium carbonate as a corrosion inhibitor in an anti-freeze or other cooling system fluid. The inhibitor is present as 0.05 to 2.0 weight percent of the fluid. U.S. Pat. 2,281,401 discloses use of oil soluble metal salts of phenol and naphthol. U.S. Pat. 2,347,152, 2,381,912, and 2,321,576 are several of the many patents disclosing metal phenoxides. U.S. Pat. 3,159,576 discloses quaternary ammonium compounds as stiffening agents in greases, while U.S. Pat. 2,344,886 discloses such compounds as additives in low concentrations in lubricating oils. U.S. Pat. 2,739,168 discloses guanidinium salts of N-substituted maleamic acids. U.S. Pat. 2,417,441 discloses a preparation scheme for the production of certain guanidinium salts. Other

patents disclosing specific guanidinium salts include U.S. Pat. 2,580,881 and 3,158,647.

SUMMARY

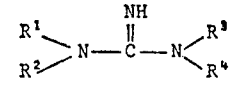
The composition of this invention is a functional fluid comprising a hydrocarbon base oil and 0.1–50 percent by weight of an oil-soluble guanidinium phenoxide or naphthoxide. The invention also includes novel guanidinium phenoxides and naphthoxides.

DETAILED DESCRIPTION OF THE INVENTION

In its broadest form, the composition of this invention is a functional fluid comprising a hydrocarbon base oil and 0.1–50 percent by weight of an oil-soluble guanidinium phenoxide or naphthoxide. The guanidinium phenoxide or naphthoxide serves as both a base reserve additive and as an anti-oxidant.

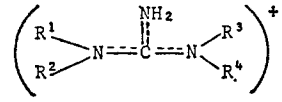
Throughout this specification, the following definitions will be used:

"Guanidine" will, unless specifically restricted to the compound $H_2N—C(:NH)—NH_2$, include substituted guanidines and will be considered to have the formula:



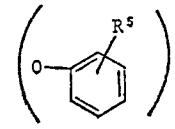
(I)

"Guanidinium" indicates a cation having the formula:



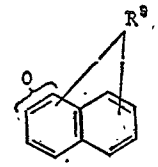
(II)

"Phenoxide" indicates a salt of phenol and is represented by the anionic formula:



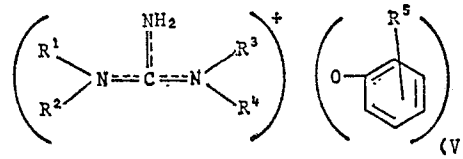
(III)

"Napthoxide" indicates a salt of α- or β- napthol and is represented by the anionic formula:



(IV)

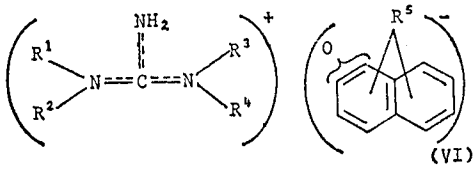
"Guanidinium phenoxide" indicates a guanidinium salt of phenol and is represented by the ionic formula:



(V)

and

"Guanidinium naphthoxide" indicates a guanidinium salt of α- or β-naphthol and is represented by the ionic formula:



(VI),

In the above formulae, R^1, R^2, R^3, and R^4 each represents a hydrogen, C_1–C_{20} alkyl, or C_6–C_{10} aryl radical, and R^5 represents 1 and 2, preferably one, hydrocarbon radicals having a total of 8–50, and preferably 8–30, carbon atoms. Because of oil solubility requirements, at least one of the radicals R^1–R^5 must be a C_{10}–C_{20} alkyl radical when any one or more of R^1–R^4 is a C_6–C_{10} aryl radical. In one preferred configuration, the C_{10}–C_{20} alkyl radical will be represented by R^5, while the C_6– C_{10} aryl radical or radicals will be among R^1–R^4. Usually not more than two of the R^1–R^4 radicals will be hydrocarbon radicals; i.e., it is preferred that at least two of the R^1–R^4 radicals be hydrogen radicals. Formulae IV and VI are meant to include both the α-naphthol and β-naphthol derivatives; the structure shown indicates that the oxygen atom may be at either the α- or β-position.

For convenience, the following definitions will be used herein. The term "hydrocarbon radical" is intended to include alkyl, aryl, and alicyclic structures. The term "aryl" includes aryl, alkaryl, and aralkyl structures. The letter *n* represents generally the class of integer superscripts in generic formulae. Thus, "R^n" may refer broadly to the class of alkyl radicals individually designated R^1, R^2, R^3, etc. Similarly, "Ar^n" refers to the class of aryl radicals individually designated Ar^1, Ar^2, Ar^3, etc.

These Formulae II through VI are meant to represent only the general structure of the compounds and the charge distribution, and should not be interpreted to indicate that the positive-charge-producing proton is attached to any specific nitrogen atom or substituent; in Formulae II, V, and VI, it is shown attached to the imino nitrogen solely for convenience and clarity of illustration.

Guanidine and substituted guanidines useful in this invention include:

Guanidine

Alkyl guanidines, including:

methyl: monomethyl guanidine, N,N-dimethyl guanidine, N,N'-dimethyl guanidine, trimethyl guanidine, tetramethyl guanidine;

ethyl: monoethyl guanidine, N,N-diethyl guanidine, N,N'-diethyl guanidine, triethyl guanidine, tetraethyl guanidine,

analogues of the C_3 through C_{20} alkyls;

N-methyl-N-ethyl guanidine
N-methyl-N'-ethyl guanidine
N-methyl-N-n-propyl guanidine
N-methyl-N-isopropyl guanidine
N-methyl-N'-n-propyl guanidine
N-methyl-N'-isopropyl guanidine
N-methyl-N,N'-diethyl guanidine
N-methyl-N',N'-diethyl guanidine
N,N-dimethyl-N'-ethyl guanidine
N,N'-dimethyl-N-ethyl guanidine
N,N-dimethyl-N',N'-diethyl guanidine
N,N'-dimethyl-N,N'-diethyl guanidine
N-methyl-N,N',N'-triethyl guanidine
N,N,N'-trimethyl-N'-ethyl guanidine

analogues of the lower alkyls up to C_{20} inclusive, having the generic formulae:

$$N—R_x—N—R_y \text{ guanidine} \quad \text{(VII)}$$

$$N—R_x—N'—R_y \text{ guanidine} \quad \text{(VIII)}$$

$$N,N—diR_x—N'—R_y \text{ guanidine} \quad \text{(IX)}$$

$$N,N'—diR_x—N'—R_y \text{ guanidine} \quad \text{(X)}$$

$$N,N,N'—triR_x—N'—R_y \text{ guanidine} \quad \text{(XI)}$$

$$N,N—diR_x—N',N'—diR_y \text{ guanidine} \quad \text{(XII)}$$

$$N,N'—diR_x—N,N'-diR_y \text{ guanidine} \quad \text{(XIII)}$$

N-methyl-N-ethyl-N'-isopropyl guanidine
N-methyl-N'-ethyl-N-isopropyl guanidine
N-methyl-N'-ethyl-N'-isopropyl guanidine
N'-methyl-N-ethyl-N'-isopropyl guanidine
N-methyl-N-ethyl-N'-isopropyl-N'-n-propyl guanidine
N-methyl-N'-ethyl-N-isopropyl-N'-n-propyl guanidine

analogues of the C_1–C_{20} alkyls having the generic formulae:

$$N—R_x—N—R_y—N'—R_z \text{ guanidine} \quad \text{(XIV)}$$

$$N—R_w—N—R_x—N'R_y—N'—R_z \text{ guanidine} \quad \text{(XV)}$$

In Formulae VII through XV, inclusive, R represents an alkyl radical and the subscripts *w*, *x*, *y*, and *z* are each integers of from 1 to 20, inclusive; they may be the same or different integers. Thus, "R_x" were $x=5$ would represent a pentyl radical (without distinction as to the particular pentyl isomer). Where one or more subscripts represent the same integer, the particular formula will have the associated N and/or N' coefficients combined and the appropriate prefix di- or tri-added. For example, if in Formula XIV *x* and *z* both are 3, the formula would represent in part the "N,N'-dipropyl" structure.

Mixed alkyl-aryl guanidines, including:

N-decyl-N'-phenyl guanidine
N-dodecyl-N-methyl-N'-phenyl guanidine
N-eicosyl-N'-phenyl guanidine
N-eicosyl-N',N'-diphenyl guanidine
N-pentadecyl-N'-tolyl guanidine
N-methyl-N-dodecyl-N'-xylyl guanidine
N-tetradecyl-N'-(p-butyl)phenyl guanidine
N-octadecyl-N'-cumyl guanidine
N-eicosyl-N',N'-dicumyl guanidine

The mixed alkyl-aryl guanidines can be represented by the formulae:

$$N—Ar^1—N—R^6—N'—R^7—N'—R^8 \text{ guanidine} \quad \text{(XVI)}$$

$$N—Ar^1—N—Ar^2—N'—R^6—N'—R^7 \text{ guanidine} \quad \text{(XVII)}$$

$$N—Ar^1—N—R^6—N'—Ar^2—N'—R^7 \text{ guanidine} \quad \text{(XVIII)}$$

$$N—Ar^1—N—Ar^2—N'—Ar^3—N'—R^6 \text{ guanidine} \quad \text{(XIX)}$$

wherein Ar^1, Ar^2, and Ar^3 each represents a C_6–C_{10} aryl structure, R^6, R^7, and R^8 each represents hydrogen or C_1–C_{20} alkyl structure, and at least one R^n in each Formula XVI–XIX represents a C_{10}–C_{20} alkyl structure. The Ar^n components may be the same or different, as may the R^n components. As before, where two or more components are the same, their N— and/or N'— coefficients will be combined and the appropriate prefix di- or tri-added.

The basic additives of this invention are prepared by reacting guanidine or one of the guanidine derivatives described above with an alkyl-substituted phenol or naphthol. There may be one or two, preferably one, alkyl substituents on the aromatic rings of the phenol or naphthol. Total carbon content of the substituted phenol or naphthol should not exceed 50, preferably 30, carbon atoms. At least one of the substituents must contain at least eight, and preferably at least twelve, carbon atoms. Preferably, these substitutents have a linear structure or a linear structure with short side chains of 1-2 carbon atoms, such as that obtained by the polymerization or

copolymerization of lower alkenes such as ethylene, propylene, and isobutylene.

Typical phenols and naphthols which may be used in this invention include:

p-n-octyl phenol
m-n-dodecyl phenol
p-n-eicosyl phenol
p-n-tricontyl phenol
p-n-pentacontyl phenol
3,5-di-n-tetradecyl phenol
p-(3-ethyldodecyl) phenol
3-n-octyl-l-naphthol
5-n-hexadecyl-l-naphthol
4-(3-methyleicosyl)-1-naphthol
5-n-tetradecyl-2-naphthol
3-n-octyl-5-n-tetradecyl-2-naphthol
3-(6'-methyldecyl)-5-n-dodecyl-l-naphthol
p-(2,4,6,8-tetramethyl undecyl) phenol
p-(2,4,6-trimethylnonyl) phenol

The guanidinum salts of this invention will have a total carbon content not exceeding 75 carbon atoms, and preferably not exceeding 50 carbon atoms. The guanidium ion preferably contains 0–2 substituents, and these are preferably aryl substitutents. Where there are two substituents, it is further preferred that they be in the N,N'- configuration.

Base oils used for the automatic transmission fluids and other functional fluids of this invention include a variety of light hydrocarbon oils, as, for example, naphthenic base, paraffin base and mixed base mineral oils, and other hydrocarbon oils, such as those derived from coal and synthetic coils, such as alkylene polymers. The compound oils suitable for use in this invention have viscosity indexes which are between 130 and 150 and preferably are in the range of 135–145. A typical base of which is employed in this invention is a light mineral oil having a viscosity of from 50 to 400 SSU at 100° F.

The guanidinium salts of the invention will be present in the fluids as 0.1 to 50 weight percent. Usually they will be present as 0.1 to 15 weight percent, but concentrations of 15–50 percent may be used in concentrates to facilitate shipping and storage. Prior to use these concentrates will normally be diluted to the lower concentration range.

The typical functional fluids in which the aforementioned additives are employed contain as a general rule a viscosity index improver, a polymeric detergent, a rust preventive agent, an oxidation inhibitor, a foam suppressant, and a dye.

The conventional additives employed in the automatic transmission fluid in addition to the above-mentioned guanidinium salts include from 1% to 15% by weight of one or more polymeric viscosity index improvers, such as mixed alkyl methacrylate polymers and polyisobutylenes. An example of a preferred viscosity index improver which may be employed in the compositions of this invention is an alkyl methacrylate-vinyl pyrrolidone copolymer. Another example of a suitable viscosity index improver is a polymerized alkyl methacrylate having an average of 12 carbon atoms in the alkyl chain and a molecular weight of about 200,000.

Suitable polymeric detergents are oil soluble copolymers of alkyl methacrylates and vinyl pyrrolidones or N-alkyl piperazines.

Suitable polymers and copolymers such as those typified by these examples with molecular weights of from 20,000 to 300,000 may be used in the compositions of this invention.

The oxidation inhibitors are normally selected from suitable diarylamines and di-(tert-butyl) phenols. Useful di-(tert-butyl) phenols include di-(tert-butyl)-p-cresol; 4,4'-methylene-bis{2,6-di-(tert-butyl) phenol}; 2,6-di-(tert-butyl)-α-dimethylamino-p-cresol; and 2,6-di-(tert-butyl) phenol. Suitable diarylamines include phenyl-α-naphthylamine, bis-(octylphenyl) amine, and N,N'-diphenyl-p-phenylene diamine. These oxidation inhibitors are employed in minor amounts, from 0.1 percent to 1 percent by weight of the composition.

The foam suppressant may be a dimethyl silicone polymer employed in amounts from 0.0008 percent to 0.01 percent by weight of base oil.

The rust preventives which are employed in the invention may be pentaerythritol monooleate, calcium petroleum sulfonate and alkenyl succinic acids.

Typical dyes used in small amounts to impart desired colors to the fluids include alkylated aniline dyes, azo dyes, or anthroquinone dyes.

The following examples will illustrate the preparation of typical guanidine additives of this invention. "Polypropylene" indicates a mixture of C_{12}–C_{14} alkyl groups derived from propylene monomer.

EXAMPLE 1

One mole of a commercial guanidine hydrochloride was dissolved in a 5:6 volumetric mix of methanol and ethanol. This was then reacted with 1 mole of p-polypropylene phenol and 1 mole of potassium hydroxide as a 40 percent solution in methanol. The reaction took place at ambient temperature. Guanidinium p-polypropenyl phenate was recovered.

EXAMPLE 2

One-half mole of N,N,N',N'-tetramethyl guanidine was reacted with ½ mole of p-polypropylene phenol. During the exothermic reaction, the temperature rose from ambient to 54° C. N,N,N',N'-tetramethyl guanidinium p-polypropylene phenate was recovered.

EXAMPLE 3

A solution of 0.1 mole of p-polypropylene phenol in methanol was reacted with 0.1 mole of N,N'-di-o-tolyl guanidine at a temperature of 50° C. N,N'-di-o-tolyl guanidinium p-polypropylene phenate was recovered.

The base reserve additives described in the above examples were incorporated into a conventional automatic transmission fluid having the formulation:

	Volume percent
Blend of neutral and pale hydrocarbon oils	90.4
Alkyl methacrylate/vinyl pyrrolidone polymer	3.0
High molecular weight polyisobutylene	3.0
Diisobornyl diphenyl amine	1.0
Zinc dioctyl dithiophosphate	0.5
Calcium sulfonate	2.1

Each fluid described in the table below was tested in an oxidation test to determine its viscosity increase under the test conditions. In the oxidation test, the samples were placed in glass tube containing coils of steel and copper wire as catalysts, and air was bubbled through the solutions. The test was continued for 350 hours at a temperature of 325° F. The concentration of the guanidine or calcium base reserve agent was 200 meq./kg. in each case. Data from these tests are presented in the table below.

TABLE I

Base reserve agent	Concentration, weight percent	Viscosity at 210° F., SUS		Viscosity increase, percent
		Before	After	
None		51	[a] +205	[a] +300
Calcium polypropylene phenate	10	50	[b] 194	290
Guanidinium polypropylene phenate (Ex. 1)	6.4	54	61	14
N,N,N',N'-tetramethyl guanidinium polypropylene phenate (Ex. 2)	7.2	50	164	230
N,N'-di-o-tolyl guanidinium polypropylene phenate (Ex. 3)	10	50	69	38

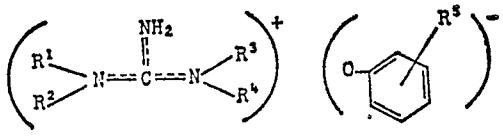
[a] Stopped at 230 hours because of excessive viscosity increase.
[b] Gelatinous at room temperature.

It is evident from these data that the incorporation of guanidinium salts in automatic transmission fluids significantly decreases the degree of viscosity increase of the fluid under oxidizing conditions. The degree of improvement is especially marked for those fluids containing the preferred guanidinium salts having 0–2 substituents on the cation. Further, in all cases, the guanidinium salts showed none of the gelation found with the calcium salt.

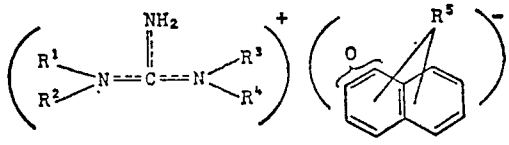
It is apparent from the data and examples above that fluids containing guanidinium phenoxide and naphthoxides exhibit markedly improved qualities. They are superior fluids for use in automatic transmissions and in other typical functional fluid applications.

We claim:

1. A hydrocarbon oil functional fluid composition comprising a hydrocarbon base oil susceptible to oxidation and in an amount of 0.1 to 50 weight percent of said fluid, as an antioxidant for said base oil, an oil-soluble guanidinium phenoxide of the formula



or a guanidinium naphthoxide of the formula



wherein each of R^1–R^4 is a hydrogen C_1–C_{20} alkyl, or C_6–C_{10} aryl radical, R^5 is one or two alkyl radicals having a total carbon content of 8–50 carbon atoms, and at least one of R^1–R^5 is a C_{10}–C_{20} alkyl radical when any one of R^1–R^4 is a C_6–C_{10} aryl radical.

2. The composition of claim 1 consisting essentially of said hydrocarbon oil and said guanidinium phenoxide.

3. The composition of claim 2 wherein said R^5 is a single C_{10}–C_{20} alkyl radical and R^1-R^4 consists of or 2 aryl C_6–C_{10} radicals and 2 or 3 hydrogen radicals.

4. The composition of claim 2 wherein said guanidinium phenoxide is present in a concentration of 0.1 to 15 weight percent of said fluid.

5. The composition of claim 1 consisting essentially of said hydrocarbon oil and said guanidinium naphthoxide.

6. The composition of claim 5 wherein said R^5 is a single C_{10}–C_{20} alkyl radical and R^1–R^4 consists of or 2 aryl C_6–C_{10} radicals and 2 or 3 hydrogen radicals.

7. The composition of claim 5 wherein said guanidinium naphthoxide is present in a concentration of 0.1 to 15 weight percent of said fluid.

References Cited

UNITED STATES PATENTS

2,344,886	3/1944	Lieber	252—51
2,739,168	3/1956	Carnes et al.	260—501
2,417,441	3/1947	Paden et al.	260—564

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U.S. Cl. X.R.

252—51.5 R, 75, 401, 403, 405; 260—501.14, 564 D, 564, 565

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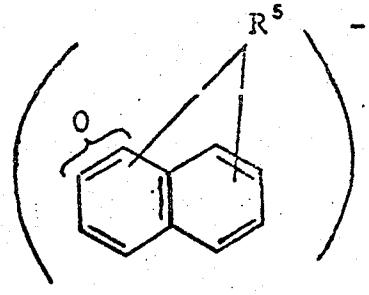
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Column 2, lines 55-60, Formula IV should read:



Column 2, line 65, Formula V should have a minus sign after the last bracket.

Column 4, line 24, "R_x were" should read --R_x where--.

Column 3, line 15, "1 and 2" should read --1 or 2--.

Column 5, line 36, "base of" should read --base oil--.

Claim 3, Column 8, line 7, "consists of or 2" should read --consists of 1 or 2--.

Claim 6, Column 8, line 15, "consists of or 2" should read --consists of 1 or 2--.

Signed and sealed this 2nd day of April 1974.

(SEAL)
Attest:

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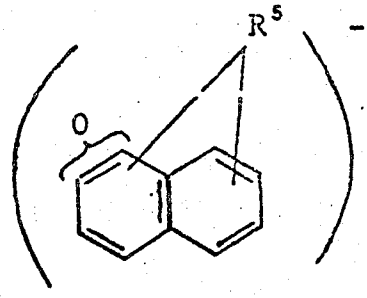
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