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3,677,943

NOVEL PHOSPHORUS-CONTAINING PYRIMIDINES AND LUBRICANTS CONTAINING SAME

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Int. Cl. C10m 1/46, 1/48
U.S. Cl. 252—46.7 9 Claims

ABSTRACT OF THE DISCLOSURE

The invention provides novel phosphorus-containing aminopyrimidines. Also provided are lubricant compositions containing these products which have improved antioxidant and extreme pressure properties.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to certain novel substituted pyrimidines, and to lubricant compositions containing same. More particularly, the invention relates to phosphorus-containing aminopyrimidines as novel compounds which have the ability to reduce oxidation and to increase extreme pressure properties of a lubricant when added thereto.

Discussion of the prior art

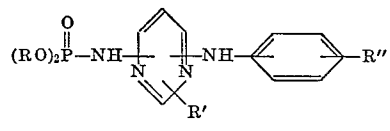
As anyone familiar with the lubrication art knows, it is rarely found that a lubricant can be used without an added compound to give it a property which may not be possessed by such lubricant in the pure state. Lubricants tend to oxidize, for example, under almost any condition when normal or elevated temperatures are involved. This is true, though to a smaller degree, even under storage conditions. At elevated temperatures, such oxidation can be particularly severe, and unless inhibited in some way the lubricating properties of the lubricant are sure to suffer from a deterioration thereof. If deterioration is not checked, the part or parts being lubricated can be seriously damaged or even rendered useless.

These faults of lubricants have been recognized by the art for many years, and there has been a constant and concerted effort to find new and more effective additives to improve such faults. As a result, there are many compounds available today for inhibiting oxidation or increasing extreme pressure properties of a lubricant.

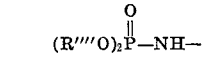
While it is known, for example, that amines and mixtures thereof may be used to inhibit oxidation in lubricants, no art is known which discloses the compounds of this invention or their use as antioxidants in such media. The closest art known is U.S. Pat. No. 3,287,453 which discloses aminopyrimidine phosphates and thiophosphates.

SUMMARY OF THE INVENTION

The invention provides new compounds of the formula



wherein R and R'' are alkyls having from 1 to 20 carbon atoms, —NH—Ar—R''' wherein Ar is phenyl or naphhydrogen, halo (i.e., chloro, bromo, iodo, fluoro and the like), nitro, amino, mercapto, hydroxy, alkoxy and alkyl, wherein the latter two have from 1 to about 20 carbon atoms, —NH,—Ar—R''' wherein Ar is phenyl or naphthyl and R''' is the same as R'', and



wherein R'''' is the same as R.

Also provided are lubricant compositions comprising a major amount of a lubricant and an antioxidant or extreme pressure amount of the above compound.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The halopyrimidines used in this invention may contain one, two or three halo groups. Thus the amount of phosphorus compound and amine required, as well as the pyrimidine to be used, will be governed by the number and kind of substituents desired on the pyrimidine nucleus. It is generally preferred that the ratio of substituents on the pyrimidine nucleus be in the relationship of whole numbers to each other. Accordingly, there may be 1 or 2 phospho groups and 1 to 2 amino groups on the nucleus.

It is contemplated that a different ratio of amino and phospho reactants may be used so long as the amounts present are at least equivalent to the amount of halo present on the pyrimidine. Thus, if two equivalents of chlorine are available for reaction, there may be 0.1 equivalent of the phosphoroamidate (or of the amine) and 1.9 equivalent of the amine (or of the phosphoroamidate).

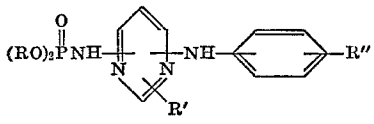
While there may be methods equally as effective, it is preferred in the practice of this invention to make the phospho pyrimidines of this invention in a single step from a halopyrimidine and the appropriate phosphorus compound and amine. This is outlined in detail in the specific examples.

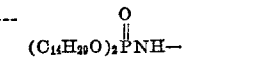
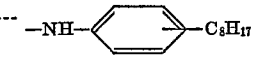
The temperature of reaction is not critical, and may be varied over a wide range, the exact temperature being governed by the reactivity of the starting materials and the degree of substitution desired. In general, the reactions can be successfully carried out from room temperature to about 250° C. Preferably, most reactions will be run at a temperature within the range of from about 80° C. to about 180° C.

The selection of a solvent apparently is routine, since no unusual effect from those solvents used were noted. Thus in selecting a solvent, the solubility of the reactants therein, as well as its ease of removal from the reaction system should be considered. Other things, such as whether the product is soluble or insoluble in the solvent will be considered by those skilled in this art.

As examples of useful solvents there may be mentioned benzene, toluene and chlorobenzene, as well as other aromatics and alkylaromatics. Also, it will be evident to those skilled in the art that tertiary amines, since they have no reactive hydrogen atom, may be used.

Included among those compounds coming within the above generic formula and which can be prepared by the general and specific procedures outlined herein are the following:



R	R′	R″
CH_3	NO_2	C_2H_5
C_2H_5	NH_2	C_6H_{13}
C_4H_9	SH	C_8H_{17}
C_8H_{17}	Cl	$C_{10}H_{21}$
C_8H_{17}	OH	C_2H_5
C_9H_{19}	OC_2H_5	C_8H_{17}
$C_{14}H_{29}$		$C_{18}H_{37}$
$C_{18}H_{37}$		C_8H_{17}
$C_{14}H_{29}$	$C_{12}H_{25}$	$C_{10}H_{21}$

The aminopyrimidines of this invention may be used, as has already been indicated, as antioxidants for lubricants. When so used, the amount thereof which will give effective antioxidant activity will range from about 0.01 to about 10% by weight of the lubricant. Preferably the amount will vary between about 0.5 and about 5% by weight.

The lubricants which may be improved by such aminopyrimidines are mineral and synthetic lubricating oils and greases made therefrom. The mineral oils will be understood to embrace not only the paraffinic, but also the naphthenic members. By synthetic oils are meant synthetic hydrocarbons, polyalkylene oxide oils, polyacetals, polysilicones and the like, as well as synthetic ester oils. Of the latter type there may be mentioned those esters made from monohydric alcohols and polycarboxylic acids, such as 2-ethylhexyl azelate and the like, and those made from polyhydric alcohols and aliphatic monocarboxylic acids. Those of this group are especially important, and they include esters prepared from the trimethylols, such as the ethane, propane and butane derivatives thereof, 2,2-disubstituted propane diols and the pentaerythritols with aliphatic monocarboxylic acids containing from about 4 to about 9 carbon atoms. Mixtures of these acids may be used to prepare the esters. Preferred in the practice of this invention are the esters prepared from a pentaerythritol and a mixture of C_5–C_9 acids. In making such esters, a generally acceptable product can be made from commercial pentaerythritol containing about 88% of monopentaerythritol and 12% dipentaerythritol.

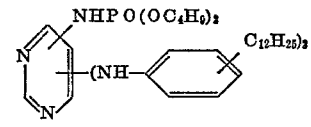
The following will specifically illustrate the invention. It will be understood that the matter is intended only for illustrative purposes, and is in no way to be construed as limiting the invention.

EXAMPLE 1

(a) Preparation of dibutylphosphoroamidate

A solution of 100 g. of dibutylphosphite in about 500 cc. CCl_4 was put in a 4 necked round bottomed flask equipped with stirrer, reflux condenser, thermometer and gas inlet tube. Then NH_3 gas was gently bubbled into the solution. The reaction temperature rose to 70° C. and formation of white crystalline material (NH_4Cl) was very visible. The NH_3 gas bubbling was continued for three hours, during which period the reaction temperature dropped to about 30° C. The white solid was filtered off, washed with 20 cc. CCl_4 and dried. The yield of NH_4Cl was 31 g. From the combined filtrate and wash solutions the solvent was removed by distillation at atmospheric pressure and the residue held at 120° C. for 2 hours under N_2 and house vacuum. The yield of light brown viscous liquid product was 108 g.

(b) To a stirred mixture of 26 g. of dodecylaniline (0.1 M), 11 g. dibutylphosphoroamidate (0.05 M) and 20 cc. N,N-dimethylaniline (to trap HCl formed) was added 9 g. 2,4,6-trichloropyrimidine (0.045 M). The reaction temperature rose to 60° C., the reaction was kept at this temperature for ½ hour and then heated at 130° C. for 5 hours. Upon cooling, the reaction product was dissolved in benzene, then filtered, and the benzene removed from the filtrate by distillation at atmospheric pressure. The residue was then held at 150° C. for 2 hours at 5 mm. Hg under N_2. The yield of thick brown gel was 43 g. The product had the following analyses: 7.53% N (theory 8.75) and 3.67% (theory 3.80). This product has the structure

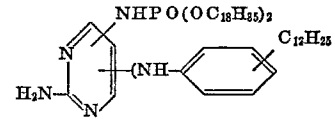


EXAMPLE 2

(a) Preparation of dioleylphosphoroamidate

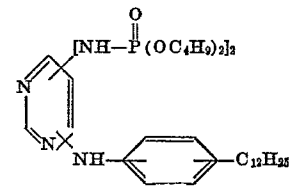
From 200 g. of dioleylphosphite reacted as shown in Example 1(a), 210 g. dioleylphosphoroamidate was obtained.

(b) A mixture of 35 g. dioleylphosphoroamidate (0.05 M) 13 g. dodecylaniline (0.05 M) and 8.2 g. 2-amino-4,6-dichloropyrimidine (0.05 M) were refluxed in 500 cc. toluene containing 20 g. N,N-dimethylaniline (to trap HCl formed) for 5 hours. It was then treated as described in Example 1(b) except that the residue after removal of toluene was held at 250° C. and 3 mm. Hg for 1 hour. In this manner 52 g. of a brown viscous material was obtained. This material contained 5.54% N (theory 7.32) and 3.29% P (theory 3.24). This material has the structure



EXAMPLE 3

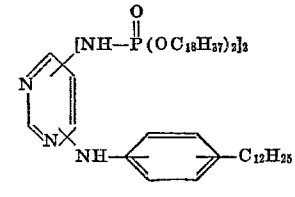
In like manner, the compound



may be prepared from trichloropyrimidine, dibutyl phosphoroamidate and dodecylaniline.

EXAMPLE 4

The compound



can be prepared in accordance with the above procedures from dioleyl phosphoroamidate, dodecylaniline and trichloropyrimidine.

EVALUATION OF PRODUCTS

As antioxidants

The compounds produced in accordance with this invention were blended into a synthetic ester oil lubricant (made by reacting pentaerythritol with an equimolar mixture of C_5 and C_9 monocarboxylic acids) and tested in an oxidation test in accordance with the following procedure.

A sample of the test composition is heated at 450° F. and air at the rate of about 5 liters per hour is passed through for a period of about 24 hours. Present in the test sample are specimens of iron, copper, aluminum, and lead. The kinematic viscosity is measured at 100° F. (percent KV change) and the change in the neutralization number (NN change). It should be noted that the metals are typical metals of engine or machine construction, and they also provide some catalysis for the oxidation or organic materials. The results are tabulated in the following table.

Inhibitor	Conc., wt. percent	NN	KV, percent 100° F.	Sludge
None		10.15	1,280	Heavy.
Example 1	2	2.89	108	Nil.
	1	4.28	168	Trace.
Example 2	2	2.15	98	Moderate.
	1	2.97	150	Trace.

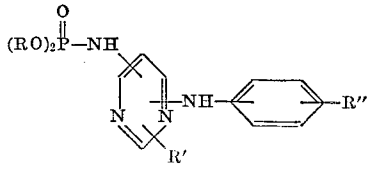
As extreme pressure agents

For EP properties, the compounds are evaluated using the well-known Four-Ball Wear Test. In this test, three stationary balls are placed in a lubricant cup and a lubricant containing the additive to be tested is added thereto. A fourth ball is placed on a chuck mounted on a device which can be used to spin the ball at known speed and loads. The data in the following table were obtained using ½" 52100 steel balls. The load was 60 kg. and the duration of the test was ½ hour. The additives were rated on the basis of reduction of wear-scar diameter of the steel balls. The lubricant is the same as above.

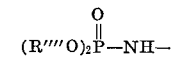
Inhibitor	Conc., wt. percent	Room temperature at— 600 r.p.m.	1,200 r.p.m.	1,800 r.p.m.
None		0.75	0.85	1.95
Example 1	1.1	0.50	0.55	1.80
Example 2	1.1	0.50	0.65	1.88

I claim:

1. A lubricant composition comprising a major proportion of a lubricating oil or grease and an amount sufficient to inhibit oxidation thereof of a compound of the formula

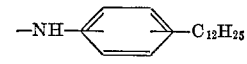


wherein R and R'' are alkyls having from 1 to 20 carbon atoms and R' is selected from the group consisting of hydrogen, halo, nitro, amino, mercapto, hydroxy, alkoxy of from 1 to about 20 carbon atoms, alkyl of from 1 to about 20 carbon atoms, —NH—Ar—R''', wherein Ar is phenyl or naphthyl and R''' is the same as R'' and



wherein R'''' is the same as R.

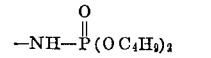
2. The composition of claim 1 wherein in the compound R is butyl, R' is



and R'' is dodecyl.

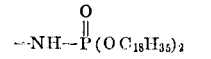
3. The composition of claim 1 wherein in the compound R is oleyl, R' is —NH_2 and R'' is dodecyl.

4. The composition of claim 1 wherein R is butyl, R' is



and R'' is dodecyl.

5. The composition of claim 1 wherein R is oleyl, R' is



and R'' is dodecyl.

6. The composition of claim 1 wherein said lubricant is a lubricating oil.

7. The composition of claim 6 wherein said lubricating oil is a synthetic ester lubricating oil.

8. The composition of claim 1 wherein said compound is present within the range of from about 0.01 to about 10% by weight.

9. The composition of claim 8 wherein said range is from about 0.5 to about 5% by weight.

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DANIEL E. WYMAN, Primary Examiner

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U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,677,943 Dated July 18,1972

Inventor(s) JOHN C. NNADI

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 2, line 2, "atoms, -NH-Ar-R''' wherein Ar is phenyl or naph-" should read --atoms and R' is selected from the group consisting of--. In column 4, line 43 (formula), " (NH- " should be -- NH- --.

Signed and sealed this 23rd day of January 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents