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3,220,898

SOLID GAS GENERATING COMPOSITIONS CONTAINING PHOSPHATE BURNING RATE SUPPRESSANTS

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This application relates to gas generating compositions, and particularly relates to the use of phosphates to suppress the burning rate of gas generating compositions.

Generally, past efforts have been directed to obtaining combustion catalysts which will increase the burning rate of gas generating compositions. However, for certain uses, particularly those wherein a long burning period is desired, and where design considerations restrict the length of the composition grain which may be used, it is desirable to reduce the burning rate of the composition, but without eliminating other desirable properties that a combustion catalyst gives, such as low temperature ignitability and combustion stability.

We have now discovered that the burning rate of gas generating compositions may be suppressed by the inclusion in the composition of a minor amount of a phosphate or amidophosphate which does not contain atoms of metals (other than, of course, phosphorous). We have also discovered that the addition of such a phosphate imparts to the composition the characteristic of producing especially clean combustion exhaust gases.

The gas generating compositions to which this invention is applicable are those in which the main constituent is ammonium nitrate. The amount of ammonium nitrate will vary widely, but it is generally in the range of about 40 to 80%, advantageously in the range of 55-70%. Commercially available ammonium nitrate, preferably in a finely divided particulate form which may be produced by prilling or grinding, is suitable. The invention may also be used in the so-called double base propellants, in which the dominant constituents are nitrocellulose and nitroglycerine.

In order to permit the shaping of the composition into definite configurations, a matrix former or binder material is incorporated into the composition. When ammonium nitrate decomposes, free oxygen is formed. Oxidizable organic materials are used as the binders in order to take advantage of the existence of free oxygen. Suitable binder materials for gas generating compositions are well known in the art. Generally, the binder includes high molecular weight hydrocarbons, such as asphalt or residuums, and/or a polymeric material, such as cellulose acetate, polyvinyl resins, including polyvinyl chloride and polyvinyl acetate, styrene-acrylonitrile, butadiene-styrene-acrylonitrile, polyurethanes, and natural or synthetic rubbers and elastomers. Frequently, a plasticizer component is included which is generally an oxygenated hydrocarbon. Illustrative plasticizers are referred to in U.S. Patent No. 3,067,075. Frequently, two or more plasticizers are used.

Suitable combustion catalysts include various organic and inorganic chromates, heavy metal cyanides, particularly Prussian blues, and alkali metal barbiturates. Such combustion catalysts are desirably included in the compositions herein claimed; merely eliminating such catalysts generally will not produce an effect comparable

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to that obtained by the inclusion of a phosphate or amidophosphate. Various burning rate promoters, such as finely divided carbon, which is not per se a combustion catalyst, are also frequently incorporated in gas generating compositions.

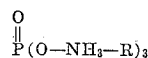
Frequently aromatic amines, such as toluene diamine and N-phenyl morpholine, may be used in minor amounts as gas evolution stabilization additives.

The phosphates which we have discovered are effective in minor amounts to suppress the burning rate of gas generating compositions, relative to the burning rate of a composition of the same ingredients in the same relative proportion but without having a phosphate, are those phosphates which are free of metal atoms, phosphorus not being considered as a metal in this sense. Preferably, the phosphates are those in which only phosphorous, oxygen, hydrogen, carbon and nitrogen atoms appear, although not necessarily all such atoms in each particular phosphate. Broadly speaking, the phosphates useful as burning rate suppressors are the organic esters and the ammonium and organic amine salts of either phosphoric acid or of amidophosphoric acids. Also included are mixed ester-amine salt phosphates and amidophosphates.

The organic esters of phosphoric acid are preferably di- and tri-esters in which the ester radicals have not more than about 24 carbon atoms per radical, such as alkyl, naphthenyls, alkenyls and mono-nuclear aryls, including their non-hydrocarbon substituted derivatives wherein the substituents are hydroxyl, nitro and amine groups. The radicals forming phosphate esters may be uniform or mixed. Illustrative of radicals which may form the esters are ethyl, isopropyl, t-butyl, allyl, hexyl, cyclohexyl, bicyclohexyl, octyl, lauryl and stearyl, phenyl, biphenyl, dinitrophenyl, cresyl, and triphenylmethyl. The phosphate esters may also be mixed according to radical type, such as alkyl-aryl, and alkyl-naphthenyl. Illustrative specific organic ester phosphates are triphenyl phosphate, tricresyl phosphate, dicyclohexyl hydrogen phosphate, isopropyl or hexyl ditridecyl phosphate, trihexyl phosphate, ethyl distearyl phosphate, dibutyl hydrogen phosphate, and dioxyhexyl nitrotolyl phosphate.

Other suitable phosphates include the triamine salts of phosphoric acid, and the mono- or diamine salts of di- or mono-esters of phosphoric acid. In addition, organic esters, amine salts or a mixed-ester amine salts of amidophosphoric acids may be used as burning rate suppressants.

Illustrative of amine salts of phosphoric acid are the salts formed by the reaction with phosphoric acid of methylamine, ethylamine, ethanol amine, hexylamine, aniline, pyridine, cyclohexylamine, and di- or trimethylamine to yield phosphates of the type



and the amine salts of diesters, such as of di(tridecyl) hydrogen phosphate, propyl octyl hydrogen phosphate, palmlyl dihydrogen phosphate, or of mono-esters. Illustrative amidophosphates are O-hexyl, O'-lauryl N-lauryl amidophosphate, the ethylamine salt of O-isopropyl N-stearyl hydrogen amidophosphate, etc.

Cyclic esters of phosphoric acid and amidophosphoric acid may also be used, such as phenyl 1,3-propyl phosphate, methyl 1,2-(butyl-4-methoxy) phosphate, triphenylmethyl 1,2-propyl phosphate, and diisopropyl N,N-ethyl-ene amidophosphate.

Additional illustrative phosphates and means of preparing them are known in literature; see, for instance, Van Wazer's "Phosphorus and Its Compounds" (1958, Interscience Publishers, Inc.), Kirk-Othmer's "Encyclopedia of Chemical Technology," volume 10 (1953), and Woodstock's U.S. Patent No. 2,406,423.

The underlying chemical common denominator of the compounds which have proven useful as burning rate suppressors is the presence of a structure



in which the three single valences or bonds of the phosphorus atoms are connected to oxygen in an ester or amine salt form, or to nitrogen in the amido form.

Only small amounts of the phosphate burning rate suppressor need be used, generally in the range of about 0.2 to 10%, advantageously in the range of about 0.5 to 2 or 3%, based on total weight of the composition. The phosphate may be added to the composition in the form of a liquid or solid; if solid, preferably in powdered or granulated form. The sequence of phosphate addition is not critical to its effectiveness, but the phosphate should be substantially uniformly dispersed throughout the composition.

A number of phosphate-containing gas generating compositions have been tested to determine their burning rate constants and pressure exponents. The compositions and test data are set forth in the table:

Table

Grain No.	1	2	3	4	5	6	7
Constituents	Composition, Weight percent						
Acetyl triethyl citrate.....	11.9	11.85	11.8	11.8	11.5	12.5	9.15
Ammonium Nitrate.....	62.5	62.30	60.0	60.0	60.0	60.0	67.35
Carbon.....	3.0	3.0	3.0	2.0	3.0	1.0	23.52
Cellulose acetate.....	10.5	10.4	12.4	12.3	12.0	12.0	8.94
Dinitrophenoxy ethanol ¹	10.6	10.45	10.8	11.4	10.5	11.0	9.04
N-phenyl morpholine.....	0.1	0.5	0.5	0.5	0.5	0.5	0.10
Sodium barbiturate.....	0.5	1.0	0.5	0.5	0.5	0.5	0.50
Toluene diamine.....	0.9	0.5	0.5	0.5	0.5	0.5	0.90
Phosphate compound.....	0	0	0.5	1.0	1.5	2.0	0.50
	Test Results						
Pressure exponent.....	.59	.65	.63	.65	.65	.73	0.65
Burning rate, inches/second:							
At 1,000 p.s.i.....	0.066	.082	0.043	.038	0.038	0.037	-----
At 700 p.s.i.....							0.058

¹ Probably containing a minor amount of dinitrophenoxy ethyl ether.

² Includes 0.25% graphite.

Grain Nos. 1 and 2 are blanks, and contain no phosphate additive. The phosphate compound of Grains Nos. 3, 4 and 5 was the diethanolic amine salt of di-tridecyl hydrogen phosphate, which may be made by neutralizing with diethanolic amine ((HOCH₂CH₂)₂NH) the product obtained by partially esterifying phosphoric acid with tridecyl alcohol. The phosphorous compound of Grain No. 6 was the lauryl amine salt of O-ethyl, N-lauryl hydrogen amidophosphate. The phosphorus compound of Grain No. 7 was tricresyl phosphate.

The table shows that the addition of small amounts of the phosphate compounds substantially reduced the burning rate of the gas generating grains relative to substantially similar compositions in which no phosphate additive was incorporated. A particularly advantageous feature of the invention resides in the fact that the exhaust combustion gases of the phosphate containing grains were cleaner than when no phosphate was used. This was determined visually by inspection of the turbine blades against which the exhaust gases were impinged.

The burning rate tests were conducted in a Crawford bomb at about 25° C.

Having thus described the invention, what is claimed is:

1. In a solid gas generating composition which comprises more than about 50% ammonium nitrate, the improvement of incorporating a member selected from the class consisting of ammonium salts, organic amine salts and organic esters of phosphoric acid and amidophosphoric acids, and mixtures thereof, said esters and organic amine salts consisting of carbon, hydrogen, nitrogen, oxygen and phosphorous atoms and having less than about 24 carbon atoms per molecule, in an amount sufficient to decrease the burning rate of said composition relative to a composition of the same ingredients having no phosphate.

2. In a solid gas generating composition which comprises more than about 50% ammonium nitrate, the improvement of incorporating a member selected from the class consisting of ammonium salts, organic amine salts and organic esters of phosphoric acid and amidophosphoric acids and mixtures thereof, said organic salts and esters having not more than about 24 carbon atoms per organic radical, in an amount sufficient to decrease the burning rate of said composition relative to a composition of the same ingredients having no phosphate, said phosphate being free of metal atoms.

3. The composition of claim 1 wherein said member is a trialkyl ester phosphate in which at least one of the alkyl groups has from 1 to about 8 carbon atoms and

in which another alkyl group has from about 12 to about 18 carbon atoms.

4. In a solid gas generating composition which comprises more than about 50% ammonium nitrate, the improvement of incorporating in the range of from about 0.2 to about 10% of a diethanolic amine salt of ditridecyl hydrogen phosphate.

5. The composition of claim 1 wherein said member is a triaryl ester phosphate.

6. The composition of claim 5 wherein said member is tricresyl phosphate.

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