

1

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NITRONIUM PERCHLORATE PROPELLANTS CONTAINING PERHALOHYDROCARBON MODIFIER

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This invention relates to a controlled burning of nitronium perchlorate mixed with a compatible hydrocarbonaceous fuel by addition of a perhalohydrocarbon in a small amount for retarding the rate of burning with minimum adverse effects on the pressure exponent and on the specific impulse of the resulting system.

Nitronium perchlorate (NO_2ClO_4), abbreviated NPC, is a potent solid oxidizer for high energy rocket propellant formulations but has given difficulties in utilization with other propellant ingredients.

Attempts to burn NPC at ordinary rocket chamber pressures with high energy fuels resulted in rapid deflagration or detonation. Pure NPC does not burn under ordinary rocket chamber pressures and a large amount of heat has to be applied for its decomposition. In U.S. patent application Ser. No. 79,946, filed Dec. 29, 1960 by H. Bieber et al., it is disclosed that NPC can be burned at a controlled rate by admixture of a small critical amount of a compatible fuel or binder, such as polyethylene, provided the said fuel is admixed in a precisely controlled amount. However, it is desirable to be able to adjust burning rate by parameters other than fuel content.

It has now been found, in accordance with the present invention, that a perhalohydrocarbon, i.e., a saturated hydrocarbon in which halogen atoms are substituted for all the hydrogen, used in a small amount, such as 0.10 to 5 wt. percent of the NPC-fuel mixture, gives a very desirable reduction of the burning rate.

The compatible fuels suitable for admixture in said small amounts with the NPC crystals are hydrocarbonaceous compounds that can be admixed with the NPC under ordinary conditions without causing appreciable reaction and which under combustion temperature and pressure conditions after ignition, promote burning of the NPC. Examples of the compatible hydrocarbonaceous fuels useful for the controlled burning of the NPC are substantially saturated hydrocarbon polymers, such as polyethylene ($-\text{CH}_2-$)_n, and other solid or semi-solid hydrocarbonaceous compounds which contain principally a saturated hydrocarbon or poly ($-\text{CH}_2-$) group, e.g., paraffin and microcrystalline waxes, saturated fatty acids, such as stearic acid, and saturated fatty esters, which contain long saturated hydrocarbon chains of polymethylene groups ($-\text{CH}_2-$)_n. Any of the hydrocarbonaceous fuel substances when admixed with the NPC will affect the rate of burning according to the energy output, in accordance with the principles set forth herein, and in U.S. app. Ser. No. 79,946. Burning rates will increase with increasing fuel content, independently of fuel type, since hydrocarbonaceous compounds have essentially the same heat of combustion on a weight basis. The hydrocarbonaceous fuel substance is preferably a polymeric material, such as polyethylene, so that it can serve also as binder of the NPC crystals. The hydrocarbon polymers having molecular weights ranging upwardly from 10,000 to 1,000,000 or higher may have only a small amount (<5%) of double bond unsaturation.

The burning rate of NPC mixed with polyethylene, or other material predominantly ($-\text{CH}_2-$) is a function of pressure and of the amount of binder.

Samples of NPC used for determining the relationship of burning rate to pressure and to polyethylene binder con-

2

centration had a particle size of 100 to 200 microns. The NPC crystals were mixed with polyethylene which has been screened through 100 mesh screens. Compressed grains of the NPC in polyethylene mixtures were made and burned under varying pressures to determine the rates of burning. The data are summarized in the following Table:

TABLE 1.—BURNING RATE OF NPC-POLYETHYLENE BINDER GRAINS AT P, PRESSURES IN P.S.I.A.

Wt. Percent Binder	Burning Rate, in./sec.			
	P=100	P=250	P=500	P=2,000
0-2	0	0	0	0
3	0.03	0.10	0.25	20
4	0.20	0.50	0.87	50
5	0.42	0.70	1.10	50
10	0.71	1.25	1.75	50

The grains of NPC with 0 to 2 wt. percent of polyethylene did not burn. At the 3 wt. percent binder level, the burning rate is extremely low at low pressure ($P=100$ p.s.i.a.), but the system has a pressure exponent greater than one indicating unstable burning. The pressure exponent, n , is the exponential variation of the burning rate, r , with pressure p in the following equation: $r=ap^n$, wherein a is a constant for any particular propellant or initial temperature.

At the 4 wt. percent polyethylene binder concentration, the pressure exponent decreased to 0.76 even through the absolute burning rate was almost a magnitude greater.

Comparison between the burning action of the grains indicates that a minimum amount of the hydrocarbonaceous fuel must be admixed for burning to supply heat for volatilization and decomposition of the NPC. Color movies of the burning grains show that at a low 2-3 wt. percent polyethylene level, burning is sporadic due to localized deficiencies of fuel and thus the high pressure exponent. At above 3 wt. percent concentration of polyethylene (well mixed with the NPC), the burning is smoother but at a higher linear rate as the pressure is increased.

There is a sharp break at 1500 p.s.i. for the grains of NPC with 4 wt. percent and 5 wt. percent polyethylene binder. This break occurs when the burning rate rises to above 2 inches per second and then becomes extremely rapid. This would indicate that a critical pressure is reached. At the 5 and 10 wt. percent polyethylene binder concentration, the pressure exponent is a satisfactory 0.57 below 1500 p.s.i.; however, the burning rate is too rapid for many applications.

Thus, it can be seen that there are practical limitations in burning the NPC with the higher concentrations of the compatible hydrocarbonaceous fuels, the limitations being extremely high burning rates often leading to detonation, especially if one tries to use a stoichiometric amount of the fuel. 84 wt. percent NPC with 16 wt. percent of polyethylene binder or similar compatible hydrocarbonaceous fuel corresponds to a stoichiometric balance for producing CO_2 and H_2O as gas products. A mixture of 63.5 wt. percent NPC and 36.5 wt. percent of compatible hydrocarbonaceous fuel is the stoichiometric balance for producing gaseous reaction products which are mainly CO and H_2 .

There is a rapid rise in burning rate as the compatible fuel binder concentration is increased to about 5 wt. percent. From 5 to 15 wt. percent of fuel binder concentration, the burning rate increase is more more gradual. From 15 to 36.5 wt. percent concentration of the compatible fuel binder, the burning rate increases slowly. Hence there are incentives for being able to control burning rate other than by variation of system stoichiometry and pressure.

As shown in the following table, although the burning rate increases as the weight proportion of hydrocarbon fuel binder ($-\text{CH}_2-$)_n admixed with NPC is increased,

the pressure exponent has reasonable values once enough fuel >3% has been added to provide smooth vaporization of the NPC.

TABLE 2.—RELATIONSHIP OF PERCENT $(-\text{CH}_2-)_n$ FUEL IN NPC TO BURNING RATE AND PRESSURE EXPONENT

Wt. percent $(-\text{CH}_2-)_n$ in NO_2ClO_4	r at 100 p.s.i.	Burning rate in./sec. at 500 p.s.i.	Pressure exponent
3.....		.25	1.36
4.....	0.25	.87	0.77
5.....	0.42	1.10	0.56
10.....	0.71	1.7	0.57
15.....	0.85	2.1	0.56
20.....	0.90		

The perhalohydrocarbons suitable as burning-rate retardants when admixed with NPC and a compatible hydrocarbonaceous fuel such as polyethylene, are typified by perhaloalkanes, such as hexafluorotetrachloropropane ($\text{C}_4\text{F}_6\text{Cl}_4$), hexachloroethane (C_2Cl_6), nonafluoropentachlorohexane ($\text{C}_6\text{F}_9\text{Cl}_5$), materials of the general form $\text{Cl}(\text{CF}_2=\text{CFCl})_x\text{Cl}$ and the like. The perhaloalkanes are compounds in which the carbons are singly bonded together in a chain and have their other valence bonds attached to halogen atoms. They may be non-volatile liquids boiling above 100°C ., waxes or solid polymers such as the polymers of chlorotrifluoroethylene.

When the perhalohydrocarbons suitable as burning-rate retardants are admixed in a minor amount with the fuel or binder, e.g., polyethylene, and the NPC, they are surprisingly effective burning-rate retardants without adverse effects on the burning rate stability indicated by a pressure exponent of less than 1 and without substantial adverse effects on the impulse of the fuel-NPC mixture.

EXAMPLE

Addition of 1 wt. percent of $\text{C}_4\text{F}_6\text{Cl}_4$ oil with 4 wt. percent polyethylene binder to NPC resulted in approximately 20% decrease in burning rate even though the pressure exponent remained nearly unchanged as is shown by measurements for the mixtures under varying pressures in the following table.

TABLE 3.—EFFECT OF $\text{C}_4\text{F}_6\text{Cl}_4$ AS BURNING RATE RETARDER IN NO_2ClO_4 +POLYETHYLENE (PE) BURNING RATE, INCHES/SECOND

Pressure, p.s.i.a.	0% $\text{C}_4\text{F}_6\text{Cl}_4$, 4% PE with NO_2ClO_4	1% $\text{C}_4\text{F}_6\text{Cl}_4$, 4% PE with NO_2ClO_4
100.....	0.258	0.219
250.....	0.485	0.404
500.....	0.900	0.724
1,000.....	1.45	1.22
Pressure Exponent, n	0.76	0.74

The proportion of the perhalohydrocarbon used as a burning rate retarder has to be sufficiently low so as not to interfere with smooth burning of the fuel and this depends on the exact composition of the hydrocarbonaceous fuel and its dispersion in the NPC.

The data in Table 2 indicate the desirability of increasing the amount of admixed fuel $(-\text{CH}_2-)_n$ in the mixture with the nitronium perchlorate if the burning rate can be retarded. Moreover, with increased proportions of the fuel $(-\text{CH}_2-)_n$, particularly in the range of 3 to 20 wt. percent, the mixture is given an increased specific impulse. Therefore, advantages are to be gained if the burning rate can be retarded while maintaining a low pressure exponent, e.g., preferably below 1 and without excessive adverse effects on the specific impulse.

However, the additive cannot be used to improve the pressure exponent. For example, if a 3% polyethylene

mixture with NPC (is in the unstable burning range) a 2 wt. percent addition of the perhalohydrocarbon $\text{C}_4\text{F}_6\text{Cl}_4$ still makes the burning unstable.

It is preferred in general to admix the perhalohydrocarbon in an amount not more than about $\frac{1}{3}$ the proportion of the hydrocarbonaceous fuel, particularly such as polyethylene or about 1-4% based on total propellant. This is to avoid excessive adverse effects of the perhalohydrocarbon on the specific impulse value of the NPC mixture.

For example, if the amount of poly $(-\text{CH}_2-)$ hydrocarbonaceous fuel, e.g., polyethylene, polypropylene, wax, petroleum resin or mixtures thereof added in a proportion of 10 to 20 wt. percent to NPC increases the burning rate to above 1 inch per second, then the proportion of perhalohydrocarbon used as burning rate retarder may be 2 to 4 wt. percent to lower the burning rate to an acceptable rate below 1 inch per second.

The NPC with admixed hydrocarbonaceous fuel and perhalohydrocarbon burning-rate retarder may be compressed into a large propellant grain to be used next to a separate grain of a monopropellant, or with sufficient fuel the NPC mixture may be used as a monopropellant. The NPC mixture containing the compatible fuel and perhalohydrocarbon may be pelleted and encapsulated, e.g. by aluminum, for distribution in a grain containing other propellant ingredients, e.g., other fuels and other oxidizing agents of high-energy values.

The invention disclosed is claimed as follows:

1. A high-impulse, modified burning-rate solid propellant composition consisting of nitronium perchlorate intimately mixed with about 3 to 20 wt. percent of polyethylene and 0.1 to 5 wt. percent of hexafluorotetrachloropropane, the proportion of the hexafluorotetrachloropropane being less than one-third that of the polyethylene.

2. A high-impulse, modified burning rate solid propellant consisting essentially of nitronium perchlorate, 4 wt. percent polyethylene and 1 wt. percent $\text{C}_4\text{F}_6\text{Cl}_4$ intimately mixed together.

3. A high impulse, modified burning rate solid propellant composition consisting essentially of nitronium perchlorate intimately mixed with about 3 to 36 wt. percent of a compatible, non-volatile, saturated hydrocarbonaceous fuel substance containing a long chain of polymethylene groups and 0.1 to 5 wt. percent of a non-volatile perhalo alkane, the perhalo alkane being less than one-third the amount of the saturated hydrocarbonaceous substance.

4. A high impulse, modified burning rate solid propellant composition consisting essentially of nitronium perchlorate intimately mixed with about 3 to 36 wt. percent of a non-volatile saturated aliphatic hydrocarbon compatible with the nitronium perchlorate and with 0.1 to 5 wt. percent of a non-volatile perhalo alkane, the perhalo alkane being less than one-third the amount of the saturated aliphatic hydrocarbon mixed with the nitronium perchlorate.

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