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THERMALLY STABLE PROPELLANT POWDERS  
CONTAINING POWDERED POLYMERIC MA-  
TERIALS AND PERCHLORATES

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The present invention relates to novel compositions of  
matter and more particularly to propellant powders which  
are stable for extended periods of time at high tempera-  
ture.

There has been a pressing need in the oil drilling in-  
dustry for propellants of high heat stability for the pur-  
pose of shattering and piercing oil well casings. Num-  
erous types of devices, commonly known as oil well  
gun perforators, have been developed for this purpose.  
Gun powder and ball powder have been used in such  
devices, but they have several serious deficiencies. Gun  
powder is relatively heat sensitive so that upon being  
lowered to great depths, premature firing and the like  
have occurred. The temperature of oil wells increases,  
of course, as the well becomes deeper. Many wells are  
now at the 12,000 to 15,000 foot level, where the tem-  
perature is in the neighborhood of 325-375° F. Presently  
the deepest ones are at the 26,000 foot level and show  
temperatures of about 465° F. The compositions of the  
prior art are unstable at temperature above 250° F. and  
thus cannot be used with reliability. Furthermore, these  
compounds require the synthesis of expensive nitro sub-  
stituted derivatives.

It is therefore an object of this invention to provide  
a novel propellant suitable for use at high temperatures.  
A further object is to provide a novel composition suitable  
for high temperature uses in oil well perforators. A still  
further object is to provide a composition useful as a  
propellant and pyrotechnic ingredient for nose cones or  
missile warheads.

The compositions of this invention are very stable at  
high temperatures for extended periods. A preferred  
composition, utilizing polyacrylonitrile, has been stored  
at temperatures above 400° F. for several months and  
has exhibited no signs of decomposition or autoignition.  
These compositions also have a low impact sensitivity in  
comparison with compositions of the prior art. They  
likewise are simpler and cheaper to prepare, as they are  
physical mixtures and thus do not require synthesis of  
expensive nitro substituted derivatives.

The compositions of this invention can be conveniently  
prepared by admixture of the ingredients. Preferred  
oxidizers are ammonium perchlorate, lithium perchlorate,  
sodium perchlorate and potassium perchlorate; while pre-  
ferred fuels are polyacrylonitrile, polyacrylamide, poly-  
N-vinylcarbazole and phenol-formaldehyde polymer.  
For best results, the fuel and oxidizer are combined in  
stoichiometric ratio. However, other ratios ranging from  
40-95 percent by weight of oxidizer and 5-60 percent  
by weight of fuel can be used. In addition, burning  
rate modifiers such as ferric oxide, ammonium dichro-  
mate, copper chromite, and ammonium ferrocene sul-  
fonate and anticaking agents such as finely divided silicon  
dioxide can be added as desired.

The compositions of this invention differ from other  
propellants in that they are not cast and cured. The  
fuels used are extremely high molecular weight com-  
pounds and are so viscous that they are considered solids.  
They can be powdered in a hammer mill, for instance.  
Further, their viscosity does not decrease upon heating.

These compositions, when ignited by suitable means

such as a squib, volatilize rapidly producing large volumes  
of gas rather slowly. The compositions do not melt  
before volatilizing. It is therefore advantageous to have  
as much surface area available as possible. The fuel  
and oxidizer can be reduced in particle size by means  
of a suitable apparatus, such as a hammer mill. One  
fuel, polyacrylonitrile, as manufactured, has a particle  
size ranging from 3 to 100 microns. This is eminently  
suited for the purpose. The other fuels and oxidizers  
must be reduced in size before they are used.

The fuel and oxidizer are stirred until a homogeneous  
mixture is obtained. The burning rate modifier and anti-  
caking agent can be omitted altogether without affecting  
the properties of the propellant. After stirring, the fuel  
and oxidizer remain as discrete particles rather than the  
fuel becoming crosslinked, as in standard propellants.  
Since the fuel is already essentially a solid, no curing  
agent is required. A small amount of plasticizer can be  
added to the mixture to aid pelletization, if desired. The  
amount of plasticizer added is dependent upon the end  
use of the composition and is easily ascertainable by one  
skilled in the art.

After preparation, the composition is pressed into a  
cartridge or other device, equipped with a squib, lowered  
into the well and fired. There are several squibs, quali-  
fied at high temperatures, available for this purpose. One  
such squib is obtainable from E. I. du Pont Company  
and is known as the S-95 squib.

It will be apparent to those skilled in the art that many  
modifications, both of materials and methods, can be  
practical without departing from the invention. The  
following examples are illustrative only, and are not to  
be construed as limiting the invention either in spirit or  
in scope. In these examples temperatures are given in  
degrees Fahrenheit (° F.) and amounts of materials in  
parts by weight.

Example 1

A mixture of 12 parts of powdered polyacrylonitrile,  
87 parts of ammonium perchlorate, 0.5 part of ferric  
oxide, and 0.5 part of finely divided silicon dioxide is  
stirred in a vertical planetary mixer for 30 minutes. A  
cover is placed over the mixing bowl so that the finely  
powdered material does not escape during mixing. The  
mixture is checked visually to see that it is homogeneous.  
The propellant composition is then removed from the  
mixer and either placed in a tool or stored until needed.

These compounds have been tested for their ability to  
power devices which are used to pierce oil well casings  
at elevated temperatures. For example, this composition  
was placed in a cartridge and fired with a squib in wells  
13,500 feet deep. The temperature was recorded at 350-  
360° F. and the tool was in this environment for periods  
up to one hour. No misfirings occurred. This com-  
position has been held at 400° F. for one month and has  
shown no signs of decomposition or autoignition. Its  
autoignition temperature is about 520° F.

Example 2

Following the procedure described in Example 1, the  
following propellant formulations are obtained.

|                                   | No. 1 | No. 2 | No. 3 | No. 4 |
|-----------------------------------|-------|-------|-------|-------|
| Polyacrylamide powder.....        | 12.0  | ----- | ----- | 12.2  |
| Poly-N-vinylcarbazole powder..... | ----- | ----- | 12.0  | ----- |
| Phenol-formaldehyde powder.....   | ----- | 12.0  | ----- | ----- |
| Lithium perchlorate.....          | ----- | 87.0  | ----- | ----- |
| Sodium perchlorate.....           | ----- | ----- | 87.0  | ----- |
| Potassium perchlorate.....        | 87.0  | ----- | ----- | 87.8  |
| Ferric oxide.....                 | 0.5   | 0.5   | 0.5   | ----- |
| Silicon dioxide.....              | 0.5   | 0.5   | 0.5   | ----- |

What is claimed is:

1. A propellant composition stable to autoignition and deformation at temperatures above 325° F., said propellant composition being an admixture of about 5 to 60 percent by weight of a thermally stable fuel binder, said fuel binder being selected from the group consisting of polyacrylonitrile, polyacrylamide and poly-N-vinylcarbazole, and 40 to 95 percent by weight of a solid perchlorate oxidizer, and up to 5 percent by weight of burning rate modifiers and anticaking agents.

2. A method of stabilizing propellant containing solid perchlorate oxidizer toward autoignition and deformation at temperatures above 325° F. comprising the steps of adding to said propellant containing solid perchlorate oxidizer component, burning rate modifier, anticaking component and the like, from about 5 to 60 percent by weight of a thermally stable fuel binder component, said thermally stable fuel binder being selected from the group consisting of polyacrylonitrile, polyacrylamide and, poly-N-vinylcarbazole and admixing said propellant components until a uniform and homogeneous propellant composition is produced.

3. A method of stabilizing ammonium perchlorate based propellants toward autoignition and deformation at temperatures above 325° F. comprising the steps of adding to 40 to 95 percent by weight of ammonium perchlorate oxidizer component from 5 to 60 percent by weight of polyacrylonitrile fuel binder, and admixing said mixed components until a uniform and homogeneous propellant composition is produced.

4. A propellant composition stable to autoignition and deformation at temperatures above 325° F., said propellant composition being an admixture of about 5 to 60 percent by weight of polyacrylonitrile fuel binder, and 40 to 95 percent by weight of ammonium perchlorate oxidizer, and up to 5 percent by weight of burning rate modifiers and anticaking agents.

5. A propellant composition stable to autoignition and deformation at temperatures above 325° F., said propellant composition being an admixture of about 5 to 60 percent by weight of polyacrylonitrile fuel binder, and 40 to 95 percent by weight of potassium perchlorate oxidizer, and up to 5 percent by weight of burning rate modifiers and anticaking agents.

6. A propellant composition stable to autoignition and deformation at temperatures above 325° F., said propellant composition being an admixture of about 5 to 60 percent by weight of polyacrylonitrile fuel binder, and 40 to 95 percent by weight of lithium perchlorate oxidizer, and up to 5 percent by weight of burning rate modifiers and anticaking agents.

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