United States Patent Office 3,108,432 Patented Oct. 29, 1963

3,108,432

METHOD OF ROCKET PROPULSION USING ORGANIC POLYPEROXIDES

Jean-Claude Balaceanu, Paris, and Geneviève Clement, Coeuilly-Champigny, France, assignors to Institut Francais du Petrole des Carburants et Lubrifiants, Paris, France

No Drawing. Filed Oct. 14, 1959, Ser. No. 846,239
Claims priority, application France Oct. 16, 1958
8 Claims. (Cl. 60—35.4)

This invention relates to improvements in fuels having high energy content and especially in rocket fuels, and more particularly to improvements in those combustible materials which are conventionally utilized in two-component chemical fuels.

Since rocket fuels are known as those combustible materials which require the higher energy content, the following description will refer more particularly to this kind of fuels. However, if will be understood that particulars of the present invention may as well be applied to any other kind of fuel requiring high energy content.

Rocket fuels are generally composed of two chemicals; one a material which yields an enormous quantity of energy upon being decomposed, and the second a very strong oxidizing agent. Examples of the energy emitter are hydrocarbons, hydrazines, and boro-hydrides; and examples of strong oxidizing agents are nitric acid, hydrogen peroxide, perchlorates, liquid ozone and liquid oxygen, the most common oxidizing agent being liquid oxygen.

In view of the fact that liquid oxygen contains no other carrier atoms, it is apparent that it constitutes a very concentrated oxidizing agent. It is easily recognized, however, that the utilization of liquid oxygen has many disadvantages due to the necessary low temperature liquefaction and concomitant storage problems in order to maintain the oxygen in the liquid state.

For many purposes the preparation and storage of liquid oxygen is so cumbersome that it is customary to utilize other strong oxidizing agents which do contain carrier atoms, such as perchlorates and hydrogen peroxide, which are normally either solid or liquid at pressures and temperatures of use. It is to be noted, however, that these latter compounds necessarily contain "dead weight" carrier atoms. This fact is important as the performance of rockets is closely connected to the ratio of weight to energy release of fuel, the lower the weight, other things being equal, the better the performance. It can be seen, therefore, that conventional oxidizing agents in rocket fuels are either difficult to prepare, handle and store up, or they are comparatively inefficient because of "dead weight."

An object of the present invention, therefore, is to improve rocket fuels by eliminating the disadvantages of the prior art fuels and by improving the performance of rockets.

Another object is to provide new fuel additives.

Still another object is to provide a method for producing polyperoxides.

Other objects and advantages of this invention will become apparent on further study of the specification and appended claims.

The objects of this invention are accomplished by utilizing a new concept in rocket fuels. Whereas prior art fuels contained a combustible material on the one hand, and an oxidizing material on the other hand, it has been discovered that great advantages can be obtained by utilizing a combustible material which also contains reactive forms of oxygen necessary for combustion. These compounds belong to the class of polyperoxides.

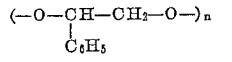
The polyperoxides can be considered as copolymers of oxygen with a polymerizable compound such as an olefinic or polyolefinic compound. They can be represented by the following general formula

$$(R_1O_2)_n$$

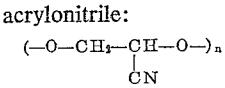
in which R_1 represents the polymerizable compound.

As examples of polyperoxides obtained from mono-olefinic compounds, the following may be used.

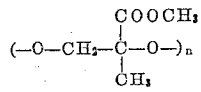
Polyperoxide of styrene:



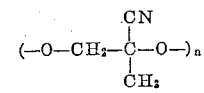
Polyperoxide of acrylonitrile:



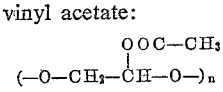
Polyperoxide of methyl methacrylate:



Polyperoxide of methacrylonitrile:



Polyperoxide of vinyl acetate:

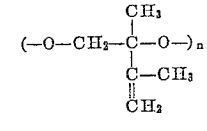


Other polyperoxides of the mono-olefins are for example:

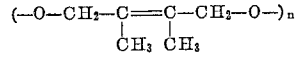
Polyperoxide of 1,1-diphenylethylene
Polyperoxide of α-methylstyrene
Polyperoxide of indene
Polyperoxide of ethylene
Polyperoxide of propylene
Polyperoxide of methylene
Polyperoxide of isobutylene
Polyperoxides of pentenes
Polyperoxide of 1,1-difluorethylene
Polyperoxide of vinylchloride

Other compounds such as the polyperoxides of the diolefins can actually be formed into several types of copolymers, the oxygen atoms being bonded to the carbon atoms in the 1,2 and/or 1,4 positions. For example, the polyperoxides of 2,3-dimethylbutadiene can be represented by the following two distinct formulae:

(a)



(b)



Likewise the polyperoxides of butadiene and of isoprene can also be represented by a plurality of configurations.

Polyperoxide of cyclopentadiene
Polyperoxide of 1,3-cyclohexadiene
Polyperoxide of α-terpinene
Polyperoxide of α-phellandrene
Polyperoxide of furan
Polyperoxide of alloocimene
Polyperoxide of chloroprene

These polyperoxides can be obtained by the reaction of oxygen on olefins and polyolefins. The reaction is advantageously conducted in the liquid phase at temperatures of about 0° to 80° C. and preferably between

35–50° C. Although the best results are obtained in that temperature range, the latter is not critical for the formation of polyperoxides, as even outside of these temperature limits polyperoxides can be formed but comparatively inefficiently. For example, it is necessary to avoid very low temperatures which would result in very low reaction rates or very high temperatures at which the compounds would decompose. The oxygen reactant is utilized in the gaseous form by itself or in mixture with an inert gas such as nitrogen. One may operate under atmospheric pressure, although under higher pressures, the reaction rate is appreciably increased.

In order to initiate the reaction or increase its rate, it is generally preferred to employ an initiator, i.e. a compound which liberates free radicals at the temperature of the reaction. Such chemical compounds may be peroxides, for example, benzoyl peroxide, reactive azo compounds, for example, azo di-isobutyronitrile, or analogs. It is obvious that one can also employ photochemical or radiochemical or other equivalent conventional reaction initiating techniques.

The obtained compounds can be isolated or concentrated by taking advantage of their physical and physicochemical properties, but it is obviously necessary to avoid such conditions which would allow their possible decomposition. Thus it is often possible to isolate them by adding to their solutions at a temperature preferably below 0° C., for example at about −30° C., such solids or liquids which reduce their solubility, for example methanol. If desired, these products may be dissolved in benzene or another aromatic solvent and re-precipitated by means of methanol, preferably below 0° C. It may also be of advantage to concentrate them by distillation or sublimation of their solvent in the cold under reduced pressure. Additional purification steps are generally unnecessary.

The above described procedures can be carried out either continuously, or by a batch process.

In order to explain this invention better, attention is directed to the following examples which however are not intended to be limitative of the appended claims.

Example I

An excess of gaseous oxygen is bubbled into styrene at temperatures from about 35–50° C. in the presence of azodiisobutyronitrile at a concentration of about 0.02 mol per liter of styrene. After 24 hours of oxygen absorption 20% of the theoretical amount of polyperoxide is obtained; the polyperoxide is precipitated by the addition of methanol at about −30° C., taken up in benzene and re-precipitated by means of methanol at the same temperature. It was then dried at 0° C. under reduced pressure (20 mm. Hg). The product thus obtained is a white solid, softening at about 50° C. and melting at about 120–130° C.

Example II

The same process as described above was successfully carried out utilizing benzoyl peroxide as an initiator.

Example III

Example I was repeated successfully employing ultraviolet light as a photochemical initiator.

Example IV

Example I was completed successfully employing the radiation of cobalt 60 as a radiochemical initiator.

Example V

In the same manner, described in Example I, a polyperoxide of acrylonitrile is formed.

Example VI

In the same manner, described in Example I a polyperoxide of methyl methacrylate is formed.

Example VII

In the same manner, described in Example I, a polyperoxide of 1,1-difluorethylene is formed.

Example VIII

In the same manner, described in Example I, a polyperoxide of vinyl acetate is formed.

Example IX

In the same manner, described in Example I, a polyperoxide of 1.1-diphenylethylene is formed.

Example X

In the same manner, described in Example I, a polyperoxide of α-methylstyrene is formed.

Example XI

In the same manner, described in Example I, a polyperoxide of indene is formed.

Example XII

In the same manner, described in Example I, a polyperoxide of dimethylbutadiene is formed.

Example XIII

In the same manner, described in Example I, a polyperoxide of cyclopentadiene is formed.

Example XIV

In the same manner, described in Example I, a polyperoxide of 1.3-cyclohexadiene is formed.

Example XV

In the same manner, described in Example I, a polyperoxide of α-terpinene is formed.

Example XVI

In the same manner, described in Example I, a polyperoxide of α-phellandrene is formed.

Example XVII

In the same manner, described in Example I, a polyperoxide of furan is formed.

Example XVIII

In the same manner, described in Example I, a polyperoxide of alloocimene is formed.

Example XIX

In the same manner, described in Example I, a polyperoxide of vinyl chloride is formed.

Example XX

A mixture of the product produced in Example I and ammonium perchlorate was ignited and found to yield a high energy release without an undesirable high weight of reactants.

Example XXI

The products described in Examples I to XIX were mixed in the same manner as described in Example XX and were also found to yield unexpectedly good results.

Example XXII

Example XX was repeated with a solution consisting of equal weights of the product produced in Example I and styrene. The energy release was substantially higher than with styrene alone.

In general, the organic polyperoxides of this invention can be utilized either as fuels per se or as additives in conjunction with other conventional fuels or oxygen-containing solid or liquid oxidants, such as perchlorates, nitric acid, hydrogen peroxide, liquid ozone and liquid oxygen. Preferably, the proportion of oxygen-containing material is chosen as to provide a substantially complete combustion of the fuel.

Since the polyperoxides of this invention have also

significant advantages as combustion-improving additives, even a very minor percentage added to a conventional fuel will be of great value.

It is considered that even a small percentage of polyperoxide within the fuel will be of some value as even a small percentage of oxygen reduces the necessary amount of other strong oxidizing compounds and facilitates the combustion. Of course, the higher the percentage of oxygen within the molecule, the more efficient will be the fuel and thus the performance of the rocket, per fuel weight unit.

Of course, these fuels are useful for propelling all types of vehicles which utilize rocket-type fuel.

It will be understood that this invention is susceptible to other modifications in order to adapt it to the different usages and conditions, such as in the process of manufacturing a polyperoxide of styrene any unreacted styrene can be recovered by vacuum distillation and used over again, and accordingly it is desired to comprehend such modifications within the invention as may fall within the scope of the appended claims.

What is claimed is:

1. In a method for propelling rockets by means of the force developed by igniting therein a chemical composition consisting of a fuel and an oxidizing agent, the improvement of adding thereto a minor amount of a polyperoxide selected from the group consisting of polyperoxides of styrene, acrylonitrile, methyl methacrylate, methacrylonitrile, vinyl acetate, 1,1-difluoroethylene, vinylchloride, 1,1-diphenylethylene, α-methylstyrene, ethylene, propylene, isobutylene and pentenes.

2. A fuel composition consisting essentially of a major amount of a chemical composition consisting essentially of a fuel and an oxidizing agent and a minor amount of polyperoxide selected from the group consisting of polyperoxides of styrene, acrylonitrile, methyl methacrylate, methacrylonitrile, vinyl acetate, 1,1-difluoroethylene, vinylchloride, 1,1-diphenylethylene, α-methylstyrene, ethylene, propylene, isobutylene and pentenes.

3. A fuel composition according to claim 2 wherein the oxidizing agent is selected from the group consisting of solid and liquid oxidizing agents.

4. A fuel composition according to claim 2 wherein the oxidizing agent is a perchlorate.

5. A fuel composition according to claim 2 wherein the oxidizing agent is nitric-acid.

6. A fuel composition according to claim 2 wherein the oxidizing agent is hydrogen-peroxide.

7. A fuel composition according to claim 2 wherein the oxidizing agent is ozone.

8. A fuel composition according to claim 2 wherein the oxidizing agent is liquid oxygen.

References Cited in the file of this patent

UNITED STATES PATENTS

2,563,305	Britton et al.	Aug. 7, 1951
2,729,936	Britton	Jan. 10, 1956
2,767,208	Miller et al.	Oct. 16, 1956
2,794,055	Russell et al.	May 28, 1957
2,795,618	Emerson et al.	June 11, 1957
2,879,276	Mayo	Mar. 24, 1959
2,896,401	Zletz	July 28, 1959
2,898,377	Handy et al.	Aug. 4, 1959
2,899,469	Jones	Aug. 11, 1959
2,911,436	Miller et al.	Nov. 3, 1959
2,971,949	Anderson et al.	Feb. 14, 1961

OTHER REFERENCES

Zaehringer: "Solid Propellant Rockets Second Stage" American Rocket Co., Box 1112 Wyandotte, Mich., 1958, pp. 207–212 and 229.