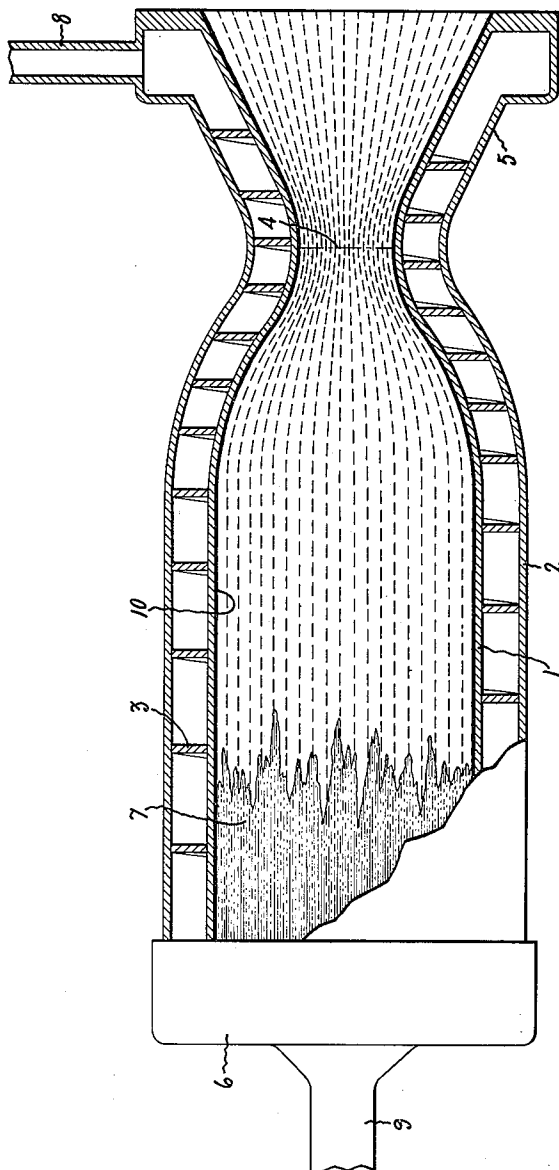


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METHOD OF OPERATING A JET PROPULSION SYSTEM
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METHOD OF OPERATING A JET PROPULSION SYSTEM

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This invention relates to jet propulsion systems. More particularly, it relates to such systems in which means is provided in the fuel for reducing the heat transfer rate to the combustor walls whereby the walls are rendered resistant to erosive conditions and are relatively long-lived.

The term jet propulsion system as used herein includes all so-called reaction type motors or engines wherein the mechanical driving thrust or force is derived from the action of equal and opposite forces arising between the motor or engine body and the body or mass of the reactants by virtue of the change in momentum of the reactants attained during the conversion of the reactants into gaseous products of greater volume than that occupied by the reactants, as distinguished from internal combustion engines of the reciprocating type. Examples of jet propulsion devices encompassed by the present invention are rocket motors, ramjets, turbojets, pulse jets, and turbo-prop-jets among others.

One of the primary problems in the design of jet propulsion or reaction type motors is that of maintaining the motor walls at relatively low temperatures with respect to the extremely high temperatures prevailing in the central portion of the combustion zone so that the walls do not rapidly burn out or erode excessively and fail. During the normal operation of a rocket motor, for example, the temperature of the combustion gases at the center of the motor is of the order of 3000° C. or even higher, with the temperature decreasing gradually toward the walls. As a practical matter, it is of the utmost importance that the temperature gradient between the hot center core and the walls be as great as feasible or that the wall temperature be as low as possible.

In an effort to protect the combustor walls against disintegration, it has been customary to build the walls of high-temperature-resisting materials and to circulate a coolant about the walls. This coolant may be one or both of the reactants later used in propelling the vehicle, or it may be a separate cooling medium such as water and the like. This method of cooling, while effective, does not go far enough in protecting the combustion chamber walls.

It has also been known to introduce a part of the fuel into the combustor through holes in the liner walls so that the vaporization of this part of the fuel absorbs heat near the walls and keeps the latter cool. This method of cooling is known variously as spray cooling, film cooling and transpiration or sweat cooling. Like the preceding method of cooling, this means of cooling is effective only to a certain degree. It has also been proposed to provide ceramic linings for the combustion chamber walls. While such linings are effective in reducing the heat transfer rate to the walls, they are easily eroded away and destroyed by the hot exit gases.

A more recently developed means of protecting the walls of jet propulsion combustors is that described in copending application Serial No. 794,672, E. H. Hull et al., filed December 30, 1947, now abandoned, and assigned to the same assignee as the present invention. In the copending application it is proposed that there be introduced into the combustion zone a substance or substances which affords therein an inorganic, non-combustible residue which is non-gaseous at temperatures adjacent the walls of the combustion zone. The residue produced is in the form of a rapidly moving cloud or screen of solid or liquid

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particles, most of which is exhausted from the combustor, with a small part depositing on the walls of the combustor as a protective coating. The rapidly moving particles form a protective screen within the combustion zone, reflecting the heat radiated from the hot central portion thereof away from the walls. That part of the screen which deposits on the walls serves as a thermal insulating coating to further protect the walls. The material may be introduced directly into the combustion zone or through its suspension or solution in one or both of the reactants.

The additive materials of the copending application comprise oxides or oxide-producing materials, the latter being typified by materials such as ethyl orthosilicate. While suspensions of oxides or oxide-producing material in the reactants or solutions of such materials are usable if freshly prepared, it has been found that the suspended material tends to settle out and clog supply lines. It has also been observed that soluble materials such as ethyl orthosilicate are very sensitive to moisture and tend to gel upon aging when added to alcohol-water or hydrocarbon fuels widely used in the reaction motor field. The presence of flux or acid in the fuel promotes such gelation. Additionally, upon standing, the alcohol or hydrocarbon in such fuel-oxide producing material combination tends to evaporate, causing the partly hydrolyzed additive to irreversibly separate out in fuel lines, valves, etc.

The copending application also mentions that oxide-producing material may be prepared from a by-product of the preparation of methylchlorosilanes as described in Patent 2,380,995, Rochow, issued August 7, 1945, and assigned to the same assignee as the present invention. After the removal of excess methyl chloride and after the isolation of methylchlorosilanes by distillation from the reaction product of silicon and methyl chloride in the presence of a catalyst such as copper, there remain in the still pot higher molecular weight organo-substituted silicon compounds containing hydrolyzable chlorine. By reaction with alcohol this chlorine can be removed in the form of HCl to leave alkoxy-substituted derivatives of the silicon compounds, which, when introduced into the combustion zone of a jet propulsion engine, produce a residue of silica therein. While such silicon-containing materials are useful in a sense, they are deficient in that, being a by-product residue, they are variable in composition from lot to lot and do not lend themselves to such precise composition control as will give reproducible results in actual use. These materials are further varying insofar as their solubility in the fuel reactant is concerned.

An object of this invention is to provide improved means for producing a heat transfer reducing medium in the combustion chambers of jet propulsion systems.

Another object of this invention is to provide new and improved materials which will provide inorganic, non-combustible residues in jet propulsion combustors or reaction motors, said materials being non-gaseous at temperatures prevailing at the walls of the combustors.

Other objects will become apparent and the invention better understood from a consideration of the following description and the drawing in which the single figure shows a rocket motor as typical of jet propulsion units.

It has been found that improved means for reducing the heat-transfer rate to the walls of jet propulsion combustors may be provided by introducing into the combustion zone a small amount of a lower molecular weight methylpolysiloxane material.

More particularly, it has been found that such means may be provided by introducing into the combustion zone a methylpolysiloxane having a molecular weight of less than about 610 or mixtures of such methylpolysiloxanes.

The methylpolysiloxanes are made up of basic organo-silicon groups connected by oxygen atoms. Such groups included within the compass of the present invention are

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the monofunctional chain-terminating group $(\text{CH}_3)_3\text{Si}-$ represented hereafter by $\text{R}_3\text{Si}-$; the difunctional chain-carrying group



represented by



and the trifunctional chain-branching group



represented by



where R is the methyl group. The methylpolysiloxanes herein may further be of the linear, branched, or cyclic type.

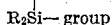
The methylpolysiloxanes of this invention are possessed of various advantageous characteristics in addition to their characteristic of forming a non-gaseous, inorganic, heat-transfer rate reducing residue in the combustor of jet propelled vehicles. They are non-reactive with moisture which is present in varying amounts in jet propulsion fuel. They further do not gel in the presence of water and in this respect are to be distinguished from ethyl orthosilicate and similar materials. The present materials are also non-toxic. They also have desirable low temperature fluidity and solubility characteristics.

As pointed out above, in general, methylpolysiloxanes having a molecular weight of less than about 610 are useful in the present application, including cyclic, branched as well as linear methylpolysiloxanes.

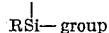
With reference to the linear methylpolysiloxanes, it has been found that compounds, and mixtures thereof, of the type wherein the ratio of



range from 2:1 to 2:5 are useful as additives for jet propulsion fuels including hydrocarbon fuels and alcohol base fuels containing water. Cyclic methylpolysiloxanes in which the

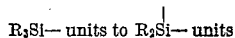


ranges from 3 to 7 have also been found useful. Branched compounds containing the



are also of use as fuel additives.

Certain materials of the present type may be used not only on nonpolar fuels but also in polar fuels such as alcohol in amounts of up to about 4 percent by weight in alcohol-water mixtures containing up to about 10 percent by weight of water. Such materials further do not separate out from such mixtures at temperatures at least as low as -60°C . even when stored for long periods of time. The materials themselves may also be stored alone at such low temperature without detrimental results. This is in contradistinction to prior art additives such as the ethyl silicates which gel and separate out at any temperature, especially on standing. Pure compounds found useful in this respect are the compound $\text{R}_3\text{Si}-\text{O}-\text{SiR}_3$ as well as those in which the ratio of



ranges from 2:1 to 2:4.

Any of the above materials when present in the fuel in amounts ranging from 1 percent to 10 percent by weight afford a silica residue in the combustion chamber which substantially reduces the heat transfer rate to the combustion chamber walls. The additive may be used

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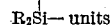
with alcohol having a water content up to 30 percent by weight.

By way of illustration, and in order to facilitate an understanding of the invention, a specific application of the method of my invention in the operation of a rocket motor is shown in the accompanying drawing. The drawing shows somewhat schematically, a rocket motor in which a portion of the inorganic non-combustible residue is being projected as a screen of moving particles through the combustion zone with the combustion gases, and another portion is being deposited as a thermal insulating coating on the walls of the motor exposed to the combustion gases.

The motor comprises an inner wall 1 and an outer wall 2 defining an annular cooling chamber. A helical member 3 located in the cooling chamber between the walls 1 and 2 provides a helical circumferential path for movement of the cooling fluid around the outside of the inner wall of the motor. Near one end of the motor the walls are restricted to form the throat 4 and an expanded section 5. At the opposite end of the walls an injection head 6 is provided for admitting the propellant fluids to the combustion chamber 7. The fuel containing silicone material affording an inorganic non-combustible residue, which is non-gaseous at temperatures prevailing adjacent the walls defining the combustion zone, enters the motor through the inlet 8 and, serving as the cooling fluid, passes through the annular chamber between the inner and outer motor walls into the injection head and then into the combustion chamber. The oxidant is admitted to the injection head through inlet tube 9. As the fuel and the oxidant react in the combustion chamber, the combustion gases pass at high velocity through the throat of the motor carrying with them a portion of the non-combustible residue in the form of small particles which reflect the heat radiated from the extremely hot central portion of the combustion zone away from the walls exposed to the combustion gases. The portion of the residue which is not exhausted with the combustion gases is deposited as a coating 10 on the inner surface of the motor. Coating 10 affords a thermal insulating coating which protects the metal wall 1 from direct contact with the combustion gases.

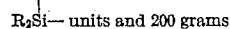
While the pure or substantially pure compounds discussed above are very useful, practical considerations such as their cost and the difficulty of obtaining them in pure form, make it advisable that mixtures of such materials be used. In general, mixtures of compounds selected from the group consisting of $\text{R}_3\text{Si}-\text{O}-\text{SiR}_3$ and compounds in which the ratio of $\text{R}_3\text{Si}-$ and $-\text{R}_2\text{Si}-$ groups ranges from 2:1 to 2:5 may be used in amounts of from 1 up to 10 percent in the present alcohol base fuels.

A useful mixture of compounds for addition to hydrocarbon or alcohol base reaction motor fuels is a mixture of methylpolysiloxanes boiling between about 200 and 300°C . obtained from the equilibration of a mixture containing from about 5 percent to 95 percent $\text{R}_3\text{Si}-$ units and about 95 percent to 5 percent



A preferred range of $\text{R}_3\text{Si}-$ units in the equilibrium mixture is 35% to 50%.

Conventional methods used for the equilibration of methylpolysiloxanes are used, the following example being indicative of the procedure. In a flask are placed 1800 grams of a methylpolysiloxane containing only



of a methylpolysiloxane containing only $\text{R}_3\text{Si}-$ units. To this is added 80 grams of concentrated sulfuric acid and 10 grams of water and the mixture is heated under reflux conditions with vigorous stirring for two hours at 100°C . to 110°C . Then 120 grams of water are added and the

reaction mixture allowed to cool to room temperature. After separation of the aqueous acid layer, the oily layer is treated with soda ash and vigorously stirred until residual traces of acid have been neutralized. This requires about 25 to 30 grams of soda ash. The solid salts are then removed by filtration. The lower molecular weight methylpolysiloxanes are separated from the equilibrated oil by fractional distillation in a high temperature Podbielniak column.

In each case the fraction having a boiling point of between 200° C. and 300° C. is selected as that most useful as a fuel additive which may be stored indefinitely at temperatures as low as -60° C. and used in hydrocarbon fuels or in alcohol base reaction motor fuels in concentrations of up to about 4 percent by weight at temperatures down to -60° C. without separation of solids. This material consists essentially of linear methylpolysiloxanes along with a small amount of cyclic methylpolysiloxanes all of a molecular weight less than about 600.

The above described materials may be advantageously used in alcohol or alcohol base fuels in amounts ranging from 1 percent to 10 percent by weight. Furthermore, the alcohol base fuel may contain up to about 10 percent by weight of water. The preferred range of additive concentration is from 2 percent to 4 percent by weight and the specific preferred additive content is 3 percent by weight. The additives may also be used in non-polar fuels such as petroleum hydrocarbon fractions, including kerosene and gasoline. Thus, I have provided a single additive which has universal application to the fuels now normally used.

As pointed out hereinbefore, the foregoing materials may be stored indefinitely at temperatures of at least -60° C. without change in composition or separation of solids. Further they may be added to pure or denatured alcohol fuels or in such fuels containing up to about 10 percent by weight of water without settling out or reacting in any way at temperatures down to at least -60° C.

While the present invention has been described with reference to particular embodiments thereof, it will be understood that numerous modifications may be made by those skilled in the art without actually departing from the invention. Therefore, I aim to cover in the appended claims all such equivalent variations as come within the true spirit and scope of the foregoing disclosure.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A method of operating a jet propulsion system in which an inorganic non-combustible residue is deposited as a thermal insulation coating on the walls of said system which comprises igniting a fuel mixture consisting essentially of (1) a combustible liquid selected from the group consisting of a petroleum fraction and an alcohol having fewer than three carbon atoms and (2) 1 to 4% of a non-gelling, non-toxic additive consisting essentially of linear methyl polysiloxanes along with a small amount of cyclic methyl polysiloxanes all of a molecular weight less than about 610, said additive having a boiling point of between 200-300° C., being capable of being stored indefinitely at temperatures as low as -60° C. without separation of solids and also capable of being dissolved in the above hydrocarbons and alcohols in concentration up to about 4% by weight at temperatures down to -60° C. without separation of solids.
2. The method of claim 1 in which the combustible liquid is an alcohol having fewer than three carbon atoms.
3. The method of claim 1 in which the combustible liquid is a mixture of ethanol and water, the water being present to an extent less than 10% by weight.
4. The method of claim 1 in which the combustible liquid is a petroleum hydrocarbon fraction.

References Cited in the file of this patent

UNITED STATES PATENTS

2,406,971	Sowa	Sept. 3, 1946
2,407,037	Sowa	Sept. 3, 1946
2,432,109	Zisman et al.	Dec. 9, 1947
2,507,422	Rust et al.	May 9, 1950
2,553,183	Caron et al.	May 15, 1951
2,563,305	Britton et al.	Aug. 7, 1951

FOREIGN PATENTS

445,506	Great Britain	Apr. 14, 1936
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OTHER REFERENCES

- Dow Corning Silicone Note Book, Fluid Series No. 3, issued September 1948, Dow Corning Corp., Midland, Mich. (Copy in Division 50.)