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GELLED FUEL COMPOSITIONS

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The present invention relates to the formation of gels, and more specifically to a novel means by which numerous normally fluid fuel compositions may be readily converted into gel form.

It is known that numerous hydrocarbons such as gasoline, kerosene, fuel oil, and lubricating oils may be readily gelled through the addition of gelling agents such as the alkali or alkaline earth metal soaps of long chain fatty acids. The resultant thickened compositions find use as lubricating greases, napalm bomb ingredients, and more recently as rocket fuels.

While the prior art soap thickening agents generally perform adequately from the standpoint of gel forming ability, it is found that the metallic soaps upon combustion leave an ash residue. For certain uses the ash residue is objectionable.

It is therefore an object of the present invention to provide a novel means for gelling normally liquid fuel compositions.

It is another object to provide a gelled liquid fuel composition which upon combustion does not leave an ash residue.

It is a further object to provide a novel fuel gelling agent which is effective for gelling a wide variety of liquid fuels, both of the hydrocarbon and non-hydrocarbon variety.

These and still further objects of the present invention will become readily apparent to one skilled in the art from the following detailed description and specific examples.

In general, the present invention contemplates a novel means for gelling normally liquid fuel compositions which comprises admixing from about 1 to about 10% by weight of a finely divided polyoxymethylene polymer with a normally liquid fuel composition. The finely divided polyoxymethylene polymer comprises finely divided fibers which possess a maximum major dimension i.e., length of about 50 microns, and a length to diameter ratio of at least 10:1.

More specifically, I have found that a wide variety of normally fluid fuel compositions may be readily gelled by the addition of about 1 to about 10% by weight of the finely divided fibrous polyoxymethylene polymer, the fibers of which are prepared by grinding a polyoxymethylene polymer which has been produced by the solid state polymerization of trioxane. The polyoxymethylene polymer which is prepared by the solid state polymerization and trioxane possesses a highly fibrous structure, and is characterized by possessing a 14 A. identity distance as measured along the fiber axis using standard X-ray crystallographic techniques. This polymer may be readily ground using conventional means to form individual fibers having a thickness (width) of below 5 microns and frequently below 1 micron. The length of the fibers are preferably below 50 microns and frequently fall in the 1 to 5 micron range. This fibrous material possesses a surprising capability of being able to form stable gels when added to numerous fuel compositions. Since the polymer is composed of repeating —CH_2O— groups and is 100% combustionable, the gelled fuel composition leaves no ash residue upon burning. Furthermore, the polymer itself possesses considerable fuel value when burned and therefore contributes for the energy content of the gelled composition.

Liquid fuels which may be treated in accordance with the teachings of the present invention are both hydrocarbon and non-hydrocarbon fuels which possess melting points below normal ambient temperatures, that is below about 0 to 25° C. Typical hydrocarbon fuels which may be gelled are those hydrocarbons of either an aliphatic or cyclic nature which possess from about 6 up to about 18 carbon atoms. Typical examples are commercially available gasoline, kerosene, fuel oils, and lubricating oil fractions. Furthermore, hydrocarbons such as benzene, toluene, and n-hexane may be treated. Non-hydrocarbon fuels such as hydrazine and substituted hydrazines including symmetrical and nonsymmetrical dimethyl hydrazine may also be effectively gelled using the novel gelling agents set forth herein.

As stated previously from about 1% to about 10% by weight based on the fuel being treated of polyoxymethylene fibers are added. It is found that this amount of fibrous polyoxymethylene will produce stable and useful gels. The precise amount of the present polyoxymethylene fibers which are added, depends somewhat on the fuel being treated and the ultimate degree of fineness of the polyoxymethylene fibers. It is generally found that the more viscous fuels such as heavy residual fuel oil or lubricating oil fractions require less polyoxymethylene fiber to provide a gel of equivalent rigidity. Furthermore, it is found that if the polyoxymethylene fibers used have been ground to a very fine degree, that is the polyoxymethylene fibers possess fiber thicknesses in the sub-micron range and maximum lengths of 1 micron or less, less polyoxymethylene fibers will produce a desired degree of thickening. In other words, it is found the gelling capability of the present polyoxymethylene fibers is generally proportional to the fiber fineness.

The present polyoxymethylene gelling agent is added to the fuel composition by conventional mixing means. That is, conventional mechanical mixers including high speed rotary blending devices and sonic generator devices may be effectively used. In general, the present polyoxymethylene fibers blend quickly and easily with the fuels being treated and no special or prolonged mixing procedure is required.

As mentioned above the polyoxymethylene used in the present invention is that obtained by the solid state polymerization of trioxane. It is found the polyoxymethylene produced by this means possesses a unique fibrous structure which is totally different than that obtained by non-solid state polymerization of formaldehyde, paraformaldehyde, or trioxane. The polyoxymethylene used in the present invention is produced most conveniently by the polymerization of a solid trioxane which has been initiated for polymerization by irradiation with high energy ionizing irradiation. A preferred mode for preparing the presently used polyoxymethylene involved (1) irradiating solid trioxane at a temperature below its melting point with high energy ionizing irradiation; (2) holding the irradiated trioxane at a temperature below its melting point preferably between 55 and about 61° C. to achieve polymerization; and (3) removing non-polymerized trioxane from the polymerization mass.

The irradiation step requires from about 0.001 to about 10 megarads of high energy ionizing irradiation to produce the required activated polymerization sites. The high energy ionizing irradiation may be comprised of high energy electrons, neutrons, deutrons, alpha particles, X-rays and gamma rays. The irradiation may be conducted either in an inert medium or in the atmosphere. However, since trioxane possesses a measurable vapor pressure at normal ambient temperatures, it is generally preferred to contain the trioxane in a closed container during the processing procedure.

The polymerization step may be conducted at any temperature in excess of 30° C. but below the melting point of the trioxane. Polymerization rate is generally depend-

ent on the temperature, therefore, a preferred temperature range for conducting the polymerization is from about 55 to 62° C. which is just below the melting point of trioxane. The polymerization step is preferably conducted in a closed container to prevent excessive loss of trioxane due to vaporization. Sufficient polymerization takes place in about 0.5 to about 10 hours, during which time a 50% conversion to polyoxymethylene may be readily obtained.

Subsequent to polymerization non-reacted trioxane, which generally comprises about 50% by weight of the polymerization mass, may be conveniently removed by evaporation or extraction with a solvent therefore, such as water, acetone, or methanol. The extracted non-reacted trioxane may be recycled back into the polymerization process after removal of solvents if used.

The polyoxymethylene polymer obtained by this method possesses a unique crystalline structure as determined by standard X-ray techniques. It is found the present polyoxymethylene possesses a 14 A. identity period along the fiber axis as compared with the 17 A. identity period found for polyoxymethylene prepared by non-solid state prior art methods. The present polymers possess a reduced specific viscosity of from about 0.3 to about 3.0 as determined by using 0.1 gram of polymer in 100 milliliters of gamma butyrolactone at 135° C. The melting point of the polymers ranges from about 185° C. to 200° C.

To obtain the finely divided fibrous material which is required for the practice of the invention, the polymers obtained from the polymerization process subsequent to purification are subjected to a grinding procedure wherein the fibrous material which is formed in cohesive bundles during the polymerization is separated and broken to the desired length. The grinding may be effected in conventional grinding or milling apparatus which include high speed rotary shearing devices, wet grinding machines, and fluid energy mills. It is generally preferred, however, to use the latter mentioned fluid energy mill to achieve the degree of grinding and size reduction required to obtain the desired fibrous gelling material.

It is found the fluid energy mill provides the grinding and milling conditions required to segregate the fibers from the bundles formed during irradiation and subsequently break them to the desired length. The fibers obtained possess a thickness or diameter of under 5 microns and preferably below 1 micron depending on the degree of fiber segregation achieved during milling. The fibers are broken to lengths of under 50 microns preferably under 5 microns during the milling operation. As mentioned previously, the gelling efficiency of the present fibrous polyoxymethylene is dependent upon the fineness of the fibrous material. The fineness of the material in turn is largely dependent on the degree of milling which is carried out. In actual practice, it is found that the highest possible degree of fiber segregation and size reduction is not carried out for economical reasons. It is frequently found that larger amounts of less finely ground material may be used more cheaply than a smaller amount of fibrous material which has been reduced to a near ultimate degree of fineness.

The gelled fuel compositions which result from the practice of the present invention find numerous uses as propellants for rockets, constituents of napalm bombs and so forth. In general, the presently gelled fuel compositions may be used for the same purposes prior art gelled fuels are used. The gelled compositions may contain other ingredients such as antioxidants, filling agents, or other additives normally found in gelled fuel compositions.

Having described the basic aspects of the present invention the following detailed examples are given to illustrate embodiments thereof.

EXAMPLE I

Commercial trioxane crystals were spread out in thin layers on trays and subjected to 0.5 megarad of 2 mev. electrons. A total of 20 kilograms of the irradiated crystals were placed in 16 oz. glass jars. The jars were sealed and submerged in a water bath heated to 55° C. The heating was continued for 5 hours. At the end of this period, the contents of the jars were extracted with water to remove the non-reacted trioxane. The dried polymer remaining after extraction with water was subsequently dried at room temperature for 24 hours. The dried product weighed 5000 grams and represented a 25% conversion. The RSV of the product was determined to be 0.9 as measured in gamma butyrolactone at 135° C. using 1/10 of the gram of the polymer in 100 milliliters of the solvent.

The dried polymer was then milled in a fluid energy mill using compressed air as the grinding medium. Milling the product at a rate of from 20 to 40 grams per minute using an injection pressure of 200 p.s.i.g. and a grinding pressure of 250 p.s.i.g. yielded a particulate fibrous product which fell within the desired particle size range.

EXAMPLE II

The fibrous polyoxymethylene obtained in Example I was admixed with JP–4 jet fuel, RP–1 fuel oil, hydrazine and unsymmetrical dimethyl hydrazine by combining the ingredients and manually stirring the mixture. In all cases it was found that 4% by weight of the fine size polyoxymethylene was sufficient to combine all the liquid into a stable gel. These mixtures remained in the form of a stable gel for a period of several weeks at room temperature.

EXAMPLE III

To illustrate the ease with which the present polyoxymethylene gelling agent may be incorporated in a liquid fuel, three different mixing procedures were used, each of which produced a different degree of agitation. (1) Fuel and the fine-size polyoxymethylene were combined and manually stirred for approximately 2 minutes. (2) Fuel and fine-size polyoxymethylene fibers were mixed together in a high speed rotating blade mixing device for 2 minutes. (3) Fuel and fibrous polyoxymethylene were mixed in sonic generator agitating device which comprised a ring-shaped transducer having a resonant frequency of 6 k.c.p.s. The results are tabulated below.

Fuel	POM (percent)	Mixing technique	Observation
JP-4	2	1, 2 and 3	Stable gel.
JP-4	4	1, 2 and 3	Do.
JP-4	10	1, 2 and 3	Do.
RP-1	2	1, 2 and 3	Do.
RP-1	5	1, 2 and 3	Do.
RP-1	9	1, 2 and 3	Do.
Hydrazine	6	1, 2 and 3	Do.
1,2 dimethyl hydrazine	5	1, 2 and 3	Do.

Microscopic examination of all of the gelled products obtained above indicated that each of the 3 mixing procedures produce substantially the same gel formation. Therefore, it is seen that any conventional mixing procedure may be effectively used.

The above specific examples clearly indicate that stable gel fuel compositions may be obtained using the fine size fibrous polyoxymethylene polymers disclosed herein. The use of the present fibrous polyoxymethylene does not require special mixing procedures, and the compositions which are formed are totally combustionable.

I claim:

1. A method for gelling liquid fuels which comprises admixing from about 1% to about 10% by weight of a finely divided fibrous polyoxymethylene polymer with a normally liquid fuel selected from the group consisting of hydrocarbons, substituted hydrocarbons, hydrazine, and substituted hydrazine, said finely divided polyoxymethylene polymer being derived from the solid state polymerization of trioxane and comprising fibers having a length of less than about 50 microns and the length to diameter ratio of at least 10:1.

2. The method of claim 1 wherein said fuel is a hydrocarbon.

3. The method of claim 1 wherein the fuel is a substituted hydrocarbon.

4. The method of claim 1 wherein the fuel is hydrazine.

5. The method of claim 1 wherein the fuel is a substituted hydrazine.

6. A gelled fuel composition comprising a normally liquid fuel selected from the group consisting of hydrocarbons, substituted hydrocarbons, hydrazine, and substituted hydrazine, and from about 1% to 10% by weight of a finely divided fiberous polyoxymethylene polymer derived from the solid state polymerization of trioxane, the fibers of said finely divided polymer possessing a major dimension of less than 50 microns and a length to diameter ratio of at least 10:1.

7. The composition of claim 6 wherein the fuel is a hydrocarbon.

8. The composition of claim 6 wherein the fuel is a substituted hydrocarbon.

9. The composition of claim 6 wherein the fuel is hydrazine.

10. The composition of claim 6 wherein the fuel is a substituted hydrazine.

11. The composition of claim 6 wherein said polyoxymethylene polymer is further characterized by possessing an identity period of 14 A. as measured along the fiber axis.

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