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GELLED FUEL AND PROCESS

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This invention relates to novel gelled heating fuels and to the process for making the same.

Gelled heating fuels have wide potential application as convenient, easily handled and comparatively safe heat sources. They can be employed in civilian use areas such as camping, outdoor cooking of all sorts, fire-starting, emergency supplies, and the like. They are essential for military use, including the heating of field rations, etc.

The most widely accepted forms of gelled heating fuels at present are ethyl alcohol gelled with a metallic soap and trioxane mixed with magnesium stearate and an organic binder. Neither of these has proved to be fully satisfactory. The trioxane tablets have a rather low caloric value of the order of about 3,200 kcal./kg. Moreover, they must be kept in tightly sealed containers to prevent excessive losses by sublimation. The ethyl alcohol formulations have a higher caloric value, typically about 7000 kcal./kg., but ethyl alcohol is a very expensive fuel and readily evaporates from the container. Moreover, it burns with a rather non-luminous flame which is not easily detected and therefore may lead to accidents, burns and fires.

In general, hydrocarbon compounds are the least expensive liquid fuels and have the highest caloric value per unit weight. However, gelled fuels prepared from liquid hydrocarbons have not heretofore been practicable because such materials burn with a smoky flame and deposit soot on cooking utensils, burner grids, etc. Accordingly, the ethyl alcohol and trioxane-based fuels have continued to be used in spite of their noted disadvantages.

It is an object of this invention to provide novel gelled heating fuels and a method for making the same. It is a further object to provide novel gelled heating fuels containing a high proportion of liquid hydrocarbons. Other objects will be apparent to those skilled in the art from the following description.

In accordance with certain of its aspects, the instant invention relates to novel gelled heating fuels comprising a normally liquid fuel containing at least one oxygenated hydrocarbon gelled with a high molecular weight polymer prepared by reacting, in said fuel, a semipolymer which is soluble therein and a chain-extending agent having at least two functionally reactive groups which are capable of reacting with at least two complementary groups in said semipolymer and wherein the normally liquid fuel contains carbon and oxygen in a ratio not greater than about 7 to 1.

In accordance with the inventions described in U.S. patent applications Ser. Numbers 54,616 and 544,618, both filed Apr. 22, 1966 in the name of Joseph Winkler, the disclosures of which are incorporated herein by reference, it is possible to prepare thixotropic gels from liquid hydrocarbons by the in situ reaction of a soluble semipolymer and a suitable chain-extending agent. It has now been discovered that these techniques are also applicable to the production of gelled heating fuels from liquid fuels containing oxygenated hydrocarbons and that such gelled compositions, when prepared as directed herein, are essentially smokeless and sootless during use. Moreover, the liquid fuels containing oxygenated hydrocarbons which can be used in the practise of this invention permit the realization of substantial cost savings which were not attainable with prior art techniques.

In accordance with these prior disclosures, gels are prepared by reacting, in the liquid to be gelled, a soluble semipolymer and a chain-extender; said chain-extender having at least two functionally reactive groups, and said semipolymer having at least two groups reactive with said functionally reactive groups. The in situ reaction further polymerizes the semipolymer to a substantially greater molecular weight, say at least 50,000 and often considerably higher. In certain preferred embodiments, the semipolymer is polymerized to a three-dimensional polymer structure, which is most conveniently effected by employing a semipolymer which is at least trifunctional and/or a chain-extender which is at least difunctional. In any case, the reaction is stopped short of the point at which the polymer formed becomes sufficiently insoluble in the liquid to precipitate therefrom.

The semipolymer employed will typically be a predominantly linear organic polymer which is soluble in the fuel to be gelled and is characterized by the presence of at least two functional groups which are reactive with complementary groups on the chain-extending agent. The molecular weight of the semipolymer may vary within wide limits and the preferred molecular weight will depend upon the particular oxygenated hydrocarbon fuel to be gelled. Normally the molecular weight will be from about 1,000 to about 10,000.

While a number of semipolymers having the above cited characteristics are available and suitable for use in preparing the compositions of this invention, the preferred semipolymers are hydrocarbon polymers, especially polyalkylenes, or polyalkylidenes containing repeating monomer units containing, for example, up to ten or more carbon atoms, and polyethers, especially polyethers derived by condensation reactions between alkylene oxides and hydroxylated alkanes each containing up to four carbon atoms. The semipolymers contain at least two reactive groups per molecule and these may be hydroxyl, thiol, carboxylic, amino, alkylamino or other reactive groups which will react with the complementary groups on the chain-extending agent. Generally the use of hydrocarbon polymers results in faster gelling compositions. On the other hand, polyether polymers are less expensive. It is possible to combine both types of polymers.

The chain-extending agent is a polyfunctional molecule containing at least two reactive groups, the exact identity of which will depend upon the functional groups in the semipolymer. Typically the chain-extender will contain at least two isocyanate, epoxy, amino or imino groups. Tolylene diisocyanate; the condensation product of bisphenol-A and epichlorohydrin available under the trademark Epon 828 from Shell Chemical Company; and the tris propylene iminephosphorous oxide product formed by reaction between the phosphorous oxychloride and propylene imine available under the trademark Mapo from Interchemical Corporation are typical chain extenders.

The preferred semipolymers are hydroxyl-terminated hydrocarbons as may be derived from butadiene or butadienestyrene copolymers, hydroxyl-terminated polyethers such as may be derived from propylene oxide or adducts of propylene oxide with glycerol, trimethylol ethane, trimethylol propane, 1,2,6-hexane triol, 1,2,4-butane triol, triethanolamine, diethylene diamine, sorbitol, methylated sucrose and the like and hydroxyl-terminated polyesters as may be derived by the reaction of polyols such as ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, glycerine, etc. with polybasic acids such as adipic acid, succinic acid, azelaic acid, dimer acids or by the self-condensation of hydroxyacids.

The preferred chain-extenders are aliphatic and aromatic polyisocyanates which are commercially available. Diisocyanates and triisocyanates are generally most suit-

able. The organic polyisocyanates which have been found most useful include tolylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hydrogenated 4,4'-diphenylmethane diisocyanate, lysine diisocyanate, polymethylene polyphenyl isocyanate, dimer acid diisocyanate and the like. The most perferred polyisocyanates are tolylene diisocyanate and hexamethylene diisocyanate. When the preferred semipolymers and chain-extenders are employed, the high molecular weight final polymer will be a polyurethane polymer.

In general, the amount of semipolymer employed will be about 3–20 parts by weight per 100 parts by weight of liquid fuel. Preferably, about 5–15 parts by weight will be employed. The chain-extender, e.g., the organic polyisocyanate, will preferably be present in amount sufficient to at least about one equivalent of isocyanate per isocyanate-reactive group. It will be understood that the precise values chosen can vary considerably depending upon the materials used and the result desired, but the above represent convenient starting points for determining the optimum values for any system.

The order in which the individual reactants are added to the fuel to be gelled can be varied to suit particular purposes. They may all be added simultaneously. If desired, the semipolymer may be pre-dissolved in the fuel and the chain-extender added thereto at the desired time. In general, it will be found most convenient to add the semipolymer to the fuel prior to chain-extender.

If desired, the reaction of the semiploymer and the chain-extender can be catalyzed with a suitable catalyst. For example, the isocyanate reaction may be catalyzed by any of the known polyurethane-forming catalysts. The catalysts are preferably soluble in the liquid fuel. Typical catalysts which may be employed as polyurethane forming catalysts include dibutyl tin dilaurate, tin octoate, ferric acetonyl acetonate, N-alkyl morpholine, triethylene diamine, tertiary piperazine derivatives and the like. The amount of catalyst will generally be small, about 0.5% to about 10% by weight, based on the weight of the semipolymer, being ordinarily sufficient.

The liquid fuels which are used in this invention will contain at least one oxygenated hydrocarbon in amount sufficient to give a carbon to oxygen ratio, in the liquid fuel, of not greater than about 7 to 1. The liquid fuel may consist entirely of one or more oxygenated hydrocarbons or it may comprise a mixture of one or more oxygenated hydrocarbons with one or more hydrocarbons, provided the carbon:oxygen atomic ratio in the liquid fuel is less than about 7:1.

It is desirable that the oxygenated hydrocarbon be free of groups which are reactive toward the chain-extender employed since reaction between the chain-extender and the oxygenated hydrocarbon would use up both materials without contributing to the formation of the desired gel. Since the preferred chain-extenders are compounds which react with active hydrogen atoms such as those contained in hydroxyl, thiol, carboxylic acid and amine groups, the oxygenated hydrocarbon should be free of these groups. In general, the oxygen in the oxygenated hydrocarbon will be in the form of an ester, ether, ketone, acetal, ketal or similar group which does not contain active hydrogen atoms.

In order to achieve the desired carbon:oxygen ratio in the liquid fuel, it is preferred that the oxygenated hydrocarbon employed have a carbon to oxygen ratio of 7 to 1 or lower, although a compound having a higher ratio may be combined with one having a lower ratio in order to arrive at the proper ratio. It is also preferred that the hydrocarbon portion of the oxygenated hydrocarbon be saturated. Finally, it is desirable that the oxygenated hydrocarbon have a boiling point of at least about 35° C. to reduce evaporation losses, boiling points in the range of 70–200° C. being especially suitable. Accordingly, the preferred oxygenated hydrocarbons are those selected from the group consisting of saturated hydrocarbon esters, ethers, ketones, acetals and ketals having a boiling point of about 70–200° C. Aliphatic esters and ethers, including cyclic ethers are especially preferred. Examples of oxygenated hydrocarbons which meet the above requirements include ethyl acetate; 1,4-dioxane; 1,3-dioxolane; diethyl carbonate; diethyl ether of ethylene glycol; dimethyl ether of diethylene glycol; trioxane, propyl acetate; butyl acetate; amyl acetate; hexyl acetate; methyl propionate; methyl butyrate; ethyl formate; diethyl ether of diethylene glycol; diethyl formal; dimethyl acetal; etc.

The liquid fuel may also contain a liquid hydrocarbon. It is preferred that the hydrocarbon be a saturated hydrocarbon having not more than about 10 carbon atoms. It should have a boiling point of at least about 35° C. to avoid excessive losses by evaporation. Preferably, it will have a boiling point in the range of from about 70° C. to about 200° C. Examples of preferred liquid hydrocarbons include heptane, octane, cyclohexane, methylcyclohexane, dimethylcyclohexane and gasoline fractions of saturated aliphatic and fully hydrogenated cycloaromatic compounds such as decahydronaphthalene.

The relative amounts of oxygenated hydrocarbon and hydrocarbon are adjusted so that the carbon to oxygen ratio in the final mixture is less than about 7 to 1. This ratio is the number of carbon atoms per oxygen atom in the fuel mixture, and is readily calculated or ascertained by elemental analysis. At ratios of 7 to 1 or lower, it is found that smoking and soot formation are drastically reduced or totally eliminated. Where the flame from the heating fuel will impinge upon a cold surface, such as a cooking utensil containing cold water, it may be desirable to use a ratio of 5 to 1 or lower to ensure that no soot will be deposited. In either case, the ratio employed may be raised somewhat if an auxiliary source of oxygen is provided in the burning area. This is most readily accomplished by providing a forced draft, venturi arrangement or the like. It is not generally necessary to use a carbon:oxygen ratio of less than about 2:1 and substantially lower values are not preferred since the caloric value per unit weight of fuel is thereby reduced.

It is a feature of the compositions of this invention that they provide an inexpensive heat source which is substantially free of smoke and soot during use. In general, they produce a luminous flame which is readily visible and therefore safer than a non-luminous flame. It is an additional feature that the compositions can be made to burn with an exceptionally quiet flame which renders them more acceptable for indoor applications and generally more pleasing to use. A quiet flame can be obtained by adding to the fuel a small amount of cellular polyurethane. A convenient source of cellular polyurethane for this purpose is the scrap or trimmings which are produced in the production of polyurethane foam products. Any type of commercially available polyurethane foam, polyester or polyether, rigid or flexible, open-cell, closed cell or reticulated, is applicable. It is preferred to add the cellular polyurethane in small pieces, preferably pieces produced by shredding the scrap to an average particle size of about 0.1 inch to about 0.5 inch. The cellular polyurethane can be added before or after gelling the fuel, but adding it before gelling is most convenient. The amount of cellular polyurethane which is added can be varied over a fairly broad range, but amounts of about 15% by weight of the total composition or less are usually adequate. Typically, the amount used will be about 2% to 10%, say 5%, of the total composition.

The gelled heating fuels are prepared by mixing together the oxygenated hydrocarbon, semipolymer, chain-extender, catalyst, hydrocarbon (if employed), cellular polyurethane (if employed), and any dyes, pigments, or fragrances which are desired to enhance the attractiveness of the product. It is preferred that the amount of water or moisture present be kept to a minimum to avoid loss of the chain-extender by side reactions and to pre-

vent corrosion of the container. However, if excessive water is present, this can be compensated for by increasing the amount of chain extender added. The reaction is permitted to proceed for the desired length of time until the proper gel is achieved. Generally, no external heat source will be necessary to initiate or maintain the reaction. Gelation will typically be complete in about several minutes to a few days, depending upon the materials and conditions. It is generally most convenient to pour the mixture into the desired container, such as cans or squeeze tubes, while still in a fluid state and then allow it to gel in the container. The gels produced possess the advantages hereinbefore noted and are highly suitable heat sources for heating, cooking and the like.

The following examples are provided to illustrate practise of specific embodiments of the instant invention. It will be understood that the invention is not limited to the specific embodiments herein set forth but encompasses all such modifications as fall within its general scope.

Example 1

Anhydrous ethyl acetate in the amount of 200 pounds is mixed with 10 pounds of the hydroxyl-terminated polyester of dimer acid and diethylene glycol having a molecular weight of about 1000 sold under the trademark Emery 3390–D. To the resultant clear solution there is added 0.2 pound of di-n-butyltin dilaurate and 0.25 pound of triethylene diamine. Finally, 2.50 pounds of tolylene diisocyanate is added and dispersed. The clear fluid is poured into cans with tight-fitting covers. Within two days, the composition forms a transparent gel which burns with a luminous, non-smoking flame.

Example 2

There is mixed together 100 pounds of anhydrous ethyl acetate, 100 pounds of commercial cyclohexane and 30 pounds of the hydroxyl-terminated polypropylene oxide-glycerol adduct having a molecular weight of about 3000 and a hydroxyl equivalent of about 1000, sold under the trademark Union Carbide LG–56. To this mixture there is added 0.2 pound of di-n-butyltin dilaurate, 0.25 pound of triethylene diamine and a small amount of a blue dye, followed by 4 pounds of tolylene diisocyanate. The resultant fluid composition is poured into aluminum squeeze tubes and allowed to gel over a period of two days to a bluish, well-set paste which is dispensed from the tube as required. The paste burns with a moderately luminous, non-smoking flame and has a caloric value in excess of about 8500 kcal./kg.

Example 3

The formulation of Example 2 is repeated except that 6.5 pounds of shredded polyester polyurethane scrap is mixed with the formulation and it is poured into cans while in a fluid state. After two days, there is obtained a gelled heating fuel composition which burns with a quiet flame.

Example 4

A clear solution is formed from 100 pounds of 1,4-dioxane and 100 pounds of commercial cyclohexane. A small amount of orange dye is added thereto, together with 0.2 pound of di-n-butyltin dilaurate, 0.25 pound of triethylene diamine, and 30 pounds of the polyether of Example 2. Finally, 4 pounds of tolylene diisocyanate are added and dispersed. The fluid composition is poured into small cans with tight-fitting covers. After one day, the composition forms a clear, orange gel which burns with a luminous, non-smoking flame and which has a caloric value of about 8600 kcal./kg.

Example 5

100 pounds of a gasoline fraction distilling over the range of 80–130° C. and which consists of a mixture of saturated aliphatic and cycloaliphatic hydrocarbons, is mixed with 100 pounds of diethyl carbonate, 0.2 pound of di-n-butyltin dilaurate, 0.25 pound of triethylene diamine, and 20 pounds of the polyester of Example 1. Finally, 5 pounds of tolylene diisocyanate are added and dispersed and the fluid composition is poured into aluminum squeeze tubes and permitted to gel to give a gelled heating paste which burns with a luminous, non-smoking flame.

Example 6

A mixture is formed from 120 pounds of the dimethyl ether of ethylene glycol, 80 pounds of decahydronaphthalene, and 30 pounds of the polyether of Example 2. There is then added 0.2 pound of di-n-butyltin dilaurate and 0.25 pound of triethylene diamine, followed by 4 pounds of tolylene diisocyanate. The fluid composition is poured into metal cans with tight covers and gels in about three days.

Example 7

120 pounds of anhydrous isobutyl acetate and 80 pounds of a gasoline fraction distilling over the range of 110–140° C. and which consists of a mixture of saturated aliphatic, cycloaliphatic, cyclohydroaromatic and naphthenic hydrocarbons, are mixed with 25 pounds of hydroxyl-terminated polyether triol having a molecular weight of about 4,000 and a hydroxyl equivalent of about 1330. To this clear mixture, there is added 0.2 pound of di-n-butyltin dilaurate and 0.25 pound of triethylene diamine, followed by 3.2 pounds of tolylene diisocyanate. The mixture is vigorously stirred for 5 minutes and one ounce of a soluble blue organic dye is added. The resultant fluid mixture is fed to an automatic filling machine into metal squeeze tubes with screw caps. After two days, the composition sets to a pasty gel which is conveniently dispensed as a heating or cooking fuel.

Example 8

200 pounds of ethyl acetate are mixed with 20 pounds of the polyether triol of Example 2. To this clear mixture, there is added 0.2 pound of di-n-butyltin dilaurate and 0.25 pound of triethylene diamine, followed by 3 pounds of tolylene diisocyanate. This composition is poured into small metal cans and gels to a thixotropic gelled heating fuel in about one day.

Example 9

A mixture is made from 100 pounds of anhydrous isopropyl acetate and 50 pounds of dry trioxane crystals. To this mixture there is added 50 pounds of a refined gasoline fraction containing only saturated aliphatic, hydroaromatic and naphthenic hydrocarbons distilling over the range of 90–110° C. There is then added, successively, 20 pounds of the polyester of Example 1, 0.2 pound of di-n-butyltin dilaurate, 0.25 pound of triethylene diamine, and 5 pounds of tolylene diisocyanate, each of which is dispersed by vigorous agitation. The resulting composition forms a soft gel in about two days and is useful as a smokeless heating and cooking fuel.

What is claimed is:

1. The process for preparing gelled heating fuels which comprises reacting, in a normally liquid fuel containing at least one oxygenated hydrocarbon which is free of functional groups reactive with organic isocyanates; a semipolymer which is soluble in said liquid fuel and has a molecular weight of at least about 1000, with a chain extending agent; said chain extending agent having at least two isocyanate functional groups per molecule; said semipolymer having at least two groups which are reactive with said isocyanate functional groups to produce a final polymer having a molecular weight substantially higher than said semipolymer, but not high enough to form a precipitate; and said liquid fuel containing carbon and oxygen in a ratio not greater than about 7:1.

2. The process of claim 1 wherein said normally liquid fuel consists essentially of an oxygenated saturated hydrocarbon having a boiling point between about 70° C. and about 200° C. and which is free of groups reactive with

the functionally reactive groups of said chain-extending agent.

3. The process of claim 1 wherein said normally liquid fuel contains a saturated hydrocarbon and an oxygenated saturated hydrocarbon both of which have a boiling point between about 70° C. and 200° C. said oxygenated hydrocarbon being free of groups which are reactive with the functionally reactive groups of said chain-extending agent.

4. A gelled heating fuel composition comprising a normally liquid fuel containing at least one oxygenated hydrocarbon which is free of functional groups reactive with organic isocyanates and a high molecular weight polyurethane formed by reaction between a semipolymer which is soluble in said liquid fuel and has a molecular weight of at least about 1000, with a chain extending agent having at least two isocyanate functional groups per molecule; said semipolymer having at least two groups which are reactive with said isocyanate functional groups; and said liquid fuel containing a carbon and oxygen in a ratio not greater than about 7:1.

5. The composition of claim 4 wherein said semi-polymer and said organic polyisocyanate are reacted in a ratio sufficient to give about one isocyanate group per hydroxyl group.

6. The composition of claim 4 wherein said normally liquid fuel consists essentially of an oxygenated saturated hydrocarbon having a boiling point between about 70° C. and about 200° C. and which is free of groups reactive

with the functionally reactive groups of said chain-extending agent.

7. The composition of claim 4 wherein said normally liquid fuel contains a saturated hydrocarbon and an oxygenated saturated hydrocarbon, both of which have a boiling point between about 70° C. and 200° C., said oxygenated hydrocarbon being free of groups which are reactive with the functionally reactive groups of said chain-extending agent.

8. The composition of claim 4 wherein there is present from about 2% to about 10% of a shredded cellular polyurethane having an average particle size of about 0.1 inch to about 0.5 inch.

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