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PROCESS FOR THICKENING LIQUID  
HYDROCARBONS

Thomas J. Kelly, Springfield, and Richard H. Rommel,  
Swarthmore, Pa., assignors to Sun Oil Company, Phila-  
delphia, Pa., a corporation of New Jersey  
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This invention relates to thickened, normally-liquid hydrocarbons, which are useful as the fuel or charge in certain devices such as incendiary missiles, flame throwers, rockets, portable cooling stoves and the like. More particularly, this invention is directed to a novel process for thickening normally-liquid hydrocarbons, and mixtures thereof such as petroleum fractions, and to the thickened compositions prepared thereby.

It is known in the art to thicken normally-liquid hydrocarbons to render them more suitable for use as fuels for certain devices requiring a semi-solid charge, such as flame throwers and incendiary missiles. In the past, this thickening process has been carried out with the aid of so-called "thickening agents," such as natural and synthetic rubber, metallic fatty acid soaps and the like. For example napalm, which found extensive use during wartime as the charge in incendiary bombs, consists of gasoline which has been thickened by the addition of a mixture of aluminum soaps of fatty acids. While the prior art thickening agents have provided satisfactory thickened fuels, they have suffered from certain other disadvantages. Foremost among these disadvantages are the relatively large proportion of thickener required to provide a suitably thickened fuel, and the very low heat of combustion of most common thickening agents. These and other disadvantages of current technology have resulted in a continuing search for new and improved thickening methods and agents.

In view of the above, a principal object of this invention is to provide a novel process for thickening normally-liquid hydrocarbons, employing a novel thickening agent, whereby thickened fuel compositions having improved properties are obtained. A further, and more specific, object of the invention, is to provide a process for thickening liquid hydrocarbons which requires the use of less thickening agent than heretofore, and which does not appreciably lessen the heating value of the resultant fuel. Another object is to provide a novel thickening agent of relatively greater effectiveness than those presently known. These and other objects and benefits will become more readily apparent from a reading of the following detailed description of the invention.

It has now been discovered that normally-liquid hydrocarbons, and mixtures thereof, can be thickened by admixture with a very small proportion of solid crystalline polypropylene in accordance with the method hereinafter described. In general, the heterogeneous admixture consisting of the liquid hydrocarbon, or mixture of hydrocarbons, and solid crystalline polypropylene, in certain proportions, is heated to an elevated temperature and vigorously agitated for a short period of time. After agitation at the elevated temperature, the now substantially homogeneous mixture is slowly cooled, with continued vigorous agitation, to an intermediate elevated temperature where the agitation is stopped. The mixture is then permitted to further cool, slowly and under quiescent conditions, to room temperature. In appearance, the product is a homogeneous, semi-solid gel which can be used, as is, in the various applications for which semi-solid fuels are employed. Polymers of other olefins, such as polyethylene and certain of the polybutenes, have been found to be completely ineffective for the instant purpose.

The liquid hydrocarbons which can be thickened in ac-

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cordance with the invention include pure hydrocarbons of any structural configuration, and mixtures of any and all such types, boiling within the range of from about 80° F. to about 950° F. at atmospheric pressure. Straight- or branched-chain paraffins and olefins, cycloparaffins and aromatic hydrocarbons can thus be thickened in accordance with this invention. Non-limiting examples of such hydrocarbons are: pentane, hexane, octane, decane, isopentane, iso-octane, triptane, pentene-1, 2-methylbutene-1, hexene-1, heptene-1, octene-1, cyclopentane, cyclohexane, benzene, toluene, xylene and the like. Various fractions of naturally-existing mixtures of hydrocarbons, such as certain fractions of petroleum, can also be satisfactorily thickened in accordance with the invention. Petroleum fractions boiling within the above-stated permissible atmospheric boiling range, including gasoline, kerosine and lubricating oil fractions, are particularly suitable for use. Gasoline fractions generally comprise mixtures of hydrocarbons boiling within the range of from about 80° F. to about 440° F., at atmospheric pressure, while kerosine has an atmospheric boiling range of from about 350° F. to about 550° F. Lubricating oil fractions of petroleum are usually designated light, medium or heavy, having atmospheric boiling ranges, respectively, of, from about 550° F. to about 750° F.; from about 525° F. to about 850° F.; and from about 575° F. to about 950° F. Mixtures of such petroleum fractions in any and all proportions can also be suitably thickened in accordance with this invention. However, it is preferred that mixtures of petroleum fractions which comprise a lubricating oil fraction should also contain gasoline, to provide the volatility characteristics required in most applications for thickened hydrocarbon fuels.

The polymers of propylene which are suitable for use in thickening liquid hydrocarbons in accordance with this invention are the solid, relatively high molecular weight, crystalline polymers of propylene, sometimes termed "isotactic" polypropylene. These polymers have a predominantly well-ordered, or regular, orientation of pendant methyl groups around asymmetric carbon atoms of a linear carbon chain. This is evidenced by their crystalline appearance under X-ray examination. Solid crystalline polypropylene is further characterized by the relatively high molecular weights of its composite polymers, which generally fall within the range of from about 30,000 to about 1,000,000, as measured by the intrinsic viscosity method. Furthermore, these polymers are substantially insoluble in the lower liquid alkanes such as, for example, the pentanes, hexanes and heptanes, at the boiling points of the latter under atmospheric pressure. Any of the above-defined solid, crystalline polymers of propylene are suitable for use in practicing this invention, although those polymers of intermediate molecular weight range, i.e., from about 50,000 or 100,000 to about 500,000 (intrinsic viscosity method), are preferred.

The solid, crystalline polypropylene employed as a thickening agent in the instant invention can be prepared, together with accompanying liquid, amorphous polymers of relatively lower molecular weight, by polymerizing the propylene with a solid, particulate catalyst maintained as a dispersion in an inert, liquid diluent, such as n-heptane or iso-octane. The solid catalyst is preferably a halide of a metal such as zirconium, chromium, vanadium, molybdenum or titanium wherein the metal is preferably in a valence state other than its highest valence state. A lower halide of titanium such as titanium trichloride or titanium dichloride is preferred. The metal halide catalyst is used with an activator therefor, such as aluminum alkyl. For example, aluminum triethyl, aluminum tri-i-propyl, aluminum tri-n-propyl, or aluminum tri-i-butyl are suitable activators and give good results. Generally, a mole ratio of activator to metal halide of from about 1:1 to about

12:1 is used. The polymerization reaction is preferably and conveniently carried on under atmospheric pressure, although elevated pressures, say up to about 10,000 p.s.i.g. (pounds per square inch gauge) can be used to advantage in that the polymerization reaction proceeds at a faster rate at such elevated pressures. Reaction temperatures of from about 32° F. to about 175° F. are suitable, although temperatures in the higher part of that range are preferred. Polypropylene containing occluded catalyst and activator is recovered from the reaction system by draining off the inert, liquid reaction medium. While not absolutely essential, it is preferred to deactivate and remove the residual catalyst by contacting the polypropylene reaction product with water, an alcohol, or an aqueous or alcoholic solution of an inorganic acid, such as nitric acid, accompanied by vigorous agitation. Preferably also, this agitation further provides for comminuting the polymer product and occluded catalyst particles during contact with the catalyst deactivating and solvent liquid. The catalyst-free product polymers are then repeatedly washed to remove at least the major portion of the residual inorganic materials, and are then dried.

Processes such as the one described above generally do not permit of close regulation of the molecular weights of the product polymers, and a mixture is normally produced, of solid, crystalline polymers and oily, or amorphous, polymers, the latter commonly termed "atactic" polymers. These amorphous polymers have molecular weights in the range of from about 5,000 to about 30,000 (intrinsic viscosity method), and are further characterized by having a predominantly statistical, or random, orientation of pendant methyl groups around the asymmetric carbon atoms of the linear carbon chain. Furthermore, they are substantially completely soluble in the lower liquid alkanes at their atmospheric boiling points. This solubility of the amorphous polymers in the hot lower liquid alkanes, particularly boiling n-pentane, provides a convenient method for selectively separating the substantially insoluble, crystalline polymers which alone are useful as a thickening agent in accordance with the present invention, from the amorphous products of propylene polymerization. It is only necessary to contact the polymer product from the polymerization step with, for example, boiling n-pentane to dissolve the amorphous polymers. The solution of amorphous polymers can then be separated from the insoluble, solid, crystalline polymers by any convenient means such as, for example, filtration. After washing with pure n-pentane, and drying, the crystalline polymers are further comminuted to a powder, and pelletized, if desirable, to provide a convenient physical form for use in the process of the invention.

While only the solid, crystalline polymers of propylene are effective as thickening agents for normally-liquid hydrocarbons in accordance with the present invention, it has been found that the presence of relatively low molecular weight, oily or amorphous polymers does not significantly interfere with the thickening process herein disclosed. Hence, for the purposes of this invention, it is not necessary to remove the amorphous polymers from the essential crystalline polymers. Propylene polymers consisting of as much as fifty percent of the amorphous variety with the essential crystalline polymers have provided satisfactory thickening when employed in accordance with the method of the invention.

In practicing the invention, the crystalline polypropylene, with or without accompanying amorphous propylene polymers, is first admixed, while agitating, with the liquid hydrocarbon or mixture of such hydrocarbons. Generally, weight ratios of hydrocarbon:thickening agent of from about 1:1 to about 20:1 are suitable, although hydrocarbon:thickening agent ratios above about 2.3:1 are preferred. After admixing the hydrocarbon and polymer, the heterogeneous mixture is slowly heated to a temperature in excess of about 180° F., but below about 270° F. if the polymer is in powdered form. When the liquid hydrocarbon

to be thickened is a predominantly saturated hydrocarbon, such as a cyclic or acyclic paraffin hydrocarbon, or is a mixture of hydrocarbons predominating in such types, excellent results are obtained when the admixture of hydrocarbon and powdered polymer is heated to a temperature only slightly in excess of 180° F. With aromatic hydrocarbons, or mixtures predominating therein, superior results are achieved when the admixture of hydrocarbon and powdered polymer is heated to temperatures in excess of about 200° F., say about 210° F. In either case, if the polypropylene is in pelletized form, it is preferred to heat the admixture to a temperature in excess of 270° F. to first dissolve the polymer. During heating, and while the admixture is at an elevated temperature, sufficient pressure should be applied to the system to prevent vaporization of the more volatile hydrocarbons. After heating, the admixture is vigorously agitated at the elevated temperature for a short period of time, say from about 5 minutes to about 45 minutes.

When the admixture of polymer and hydrocarbon has been heated and vigorously agitated at the elevated temperature, the resulting homogeneous mixture or solution is permitted to slowly cool to room temperature, with further and continuous agitation down to preferably below about 200° F. in the case of predominantly aromatic hydrocarbons, or down to preferably below about 180° F. in the case of predominantly saturated hydrocarbons. At the lower temperatures above mentioned, the agitation is stopped and the incipient semi-solid gel is permitted to further cool in a state of quiescence. Substantially all of the liquid hydrocarbon will have been incorporated in the gel, but any excess can conveniently be drained off. To obtain a gel of even drier feel, the product can be processed through parallel, separated squeeze rollers under very mild pressure. The product so obtained is in a form convenient for either storage or immediate use as a thickened hydrocarbon fuel.

In order to illustrate a specific embodiment of the invention, propylene polymers are prepared by contacting propylene at a temperature of about 160° F. and a pressure of about 150 p.s.i.g., with a dispersion of solid titanium trichloride and aluminum triethyl, the latter serving as catalyst activator, in iso-octane for a period of about 6 hours. The polymer product, after being contacted with methyl alcohol to deactivate the catalyst in accordance with preferred practice, is further contacted with boiling n-pentane under reflux conditions at atmospheric pressure to dissolve the amorphous polymers. The resulting solution of amorphous polymers in n-pentane is separated from the insoluble, crystalline polymers by filtration. The crystalline polymers are then washed with pure n-pentane and dried. These polymers are determined to have a molecular weight range of from about 50,000 to 300,000 by the intrinsic viscosity method, and to contain less than 3 percent by weight of low-molecular weight amorphous polymers. After being further comminuted to a fine powder, these crystalline polymers are ready for use as a thickening agent.

In accordance with the invention, about 1 part by weight of the above-prepared polymers is admixed with about 9 parts by weight of a gasoline consisting of a petroleum fraction boiling in the range of from about 90° F. to about 400° F. at atmospheric pressure. The admixture is agitated and heated to a temperature of about 210° F. under a pressure sufficient to maintain the liquid state. At this elevated temperature, the heterogeneous mixture is vigorously agitated for a period of about fifteen minutes. The resulting homogeneous mixture is then slowly cooled, with continuous and vigorous agitation, to a temperature of about 180° F., where the agitation is stopped and the resulting semi-solid gel is permitted to further slowly cool, under quiescent conditions, to room temperature. The resulting product gel is suitable for use as a thickened hydrocarbon fuel.

For example, the gel as above prepared is particularly

suited for use as the charge in incendiary missiles provided with means for ignition on impact. The same gel, comprising thickened gasoline, can also be employed as a solid propellant for rockets, for example, in booster rockets for airplane take-off. In the latter embodiment, an oxidizer such as aluminum or potassium perchlorate is intimately admixed with the homogeneous mixture of gasoline and crystalline polypropylene. The fuel containing the oxidizer is formed into a cylindrically-shaped semi-solid propellant "grain." This grain can be readily ignited by means of black powder initiated with electric squibs. The grain is usually burned from one end to provide a constant area of burning surface.

When other embodiments of the invention are practiced as herein described, substantially similar results are obtained.

The invention claimed is:

1. Process for preparing a semi-solid fuel composition from normally-liquid hydrocarbons which comprises: (1) admixing from about 1 to about 20 parts by weight of a liquid hydrocarbon boiling within the range of from about 80° F. to about 950° F. at atmospheric pressure with 1 part by weight of propylene polymers essentially comprising crystalline polymers having molecular weights

in the range of from about 30,000 to about 1,000,000, and which are substantially insoluble in the lower normally-liquid alkanes; (2) heating the mixture of hydrocarbon and polypropylene to a temperature above about 180° F. but below about 270° F.; (3) vigorously agitating said mixture for a short period of time; (4) cooling said mixture with agitation to a temperature between about 180° F. and about 210° F.; (5) further cooling such mixture, without agitation, to ambient temperature; and (6) recovering a semi-solid gel composed of liquid hydrocarbon and polypropylene.

2. Semi-solid fuel composition prepared in accordance with the process of claim 1.

3. Process in accordance with claim 1 wherein said liquid hydrocarbon boiling within the range of from about 80° F. to about 950° F. at atmospheric pressure is a liquid fraction of petroleum hydrocarbons boiling within the range of from about 80° F. to about 950° F. at atmospheric pressure.

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