

1

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**SOLID PRODUCT CONTAINING NORMALLY LIQUID HYDROCARBON AND NORMALLY SOLID POLYOLEFIN**

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This invention relates to a solid or rigid product containing a normally liquid hydrocarbon and a normally solid polyolefin. It also relates to a method of producing said product. In one of its aspects, the invention relates to a solid or rigid combustible fuel composition. In a further aspect of the invention, it relates to a method of preparing shaped articles from 1-olefin polymers and hydrocarbons.

The solution of minor amounts of olefin polymers, for example, polyethylene in lubricating oils, is known to frequently improve some physical properties of those oils. The product is oily in character. Similarly, polymers such as polyethylene have been used alone or with other thickening agents to convert oils into soft solids or semi-solids which are useful as lubricating greases. These polymer-containing compositions are useful since they contribute desirable properties while still retaining the liquid, syrupy, or easily deformable, or semi-solid state, which state is, in general, characteristic of the major oil components of these compositions.

The use of charcoal as a fuel for grills, barbecues and other cooking equipment for broiling, barbecuing and grilling has gained great popularity in recent years, both for indoor and outdoor facilities. This can be attributed to a substantial lowering of the cost, the convenient forms now available and the improvement in the taste of food by charcoal cooking. The most serious drawback to the use of charcoal as a source of heat in broiling food on a grill is the initial difficulty encountered in getting the charcoal to burn to the desired more or less flameless bed of coals or embers required for grilling, barbecuing or broiling purposes. The kindling point of charcoal being higher than the temperature produced by an ordinary match, some method such as saturating or pouring on a highly flammable fuel before igniting with the match has been necessary. The use of the so-called lighter fluids is not only dangerous but also expensive since much of the fluid is lost by evaporation. This has been a deterrent to many persons who otherwise would avail themselves of the advantages of charcoal broiling. Thus, it can be seen there is a distinct need for an easily ignitable fuel that produces an intense heat, which is particularly adapted for house use as a charcoal lighter or starter fuel and which is not dangerous and inconvenient to handle. The present invention relates to an easily ignitable solid fuel body, which is not dangerous or inconvenient to handle, that can be used as a starter fuel.

I have now discovered that new and useful shaped fuel compositions comprising normally liquid hydrocarbon fuels or hydrocarbon fractions and normally solid polymers can be prepared which exhibit a physical state and appearance which are, quite unexpectedly, those of the polymer alone in the sense that the composition obtained is a hard solid. Although compositions of varying degrees of hardness are obtained, the composition is at all times a

2

solid, as distinguished from the semi-solid character of a grease or the oily and syrupy liquid character of an oil.

Accordingly, it is an object of this invention to prepare a solid combustible composition derived from a normally solid polyolefin, the normally solid polyolefin constituting but a minor proportion of the product.

Further, it is an object of this invention to provide an easily ignitable fuel body of normally liquid hydrocarbons or fuels that produces an intense heat.

It is a further object of this invention to provide a method for the preparation of a normally solid, liquid hydrocarbon or fuel-containing product or body from which the liquid can be recovered.

Still further, it is an object of this invention to provide a normally solid fuel body that is substantially free of obnoxious smoke and odor while burning.

Another object of this invention is to provide an easily ignitable fuel body that because of the ease of manufacture, and the low cost of the materials, can be made available at a reasonably low cost.

A further object is to provide a coated solid fuel body adapted to be stored for long periods of time without loss of hydrocarbon fuel.

Other aspects, objects and the several advantages of this invention are apparent from a study of this disclosure and the appended claims.

According to the present invention, there are provided a solid combustible composition having an impact penetration less than about 60 percent and a method for preparation of shaped articles therefrom, the composition comprising a major proportion of a liquid hydrocarbon and a minor proportion of a normally solid high molecular weight polymer of a 1-olefin having 2-8 carbon atoms in the molecule, the method comprising essentially blending together the hydrocarbon and the high molecular weight polymer at a temperature at which an essentially uniform or homogeneous blend can be obtained, following which the solution is cooled, molded, or extruded to obtain a shaped product exhibiting the physical characteristics and appearance of the high molecular weight polymer alone.

Compositions containing as much as 95.5 weight percent liquid hydrocarbon and only about 4.5 weight percent of a particular polymer, such as polyethylene having a high molecular weight and which is normally solid in character, can be made to exhibit the physical appearance and physical state which is characteristic of the polymer alone, as described.

A solid briquet has been prepared which contains 4.5 weight percent of a high molecular weight ethylene polymer (molecular weight approximately 290,000) and about 95.5 weight percent of isoparaffinic petroleum distillate boiling between about 420 and about 475° F. This briquet is hard, non-sticky, can be handled as a solid, and yet when burned, will release about 20,000 B.t.u. per pound. Generally, the composition of the invention will contain less than about 40 percent of solid polyolefin and preferably will contain less than about 35 percent of the solid polyolefin. The compositions which have been prepared and which are now preferred, as indicated herein, contain considerably less than the upper limit which is given herein as substantially the upper limit of the invention respecting the content of solid polyolefin. The precise upper limit of solid polyolefin in the mixture will, of course, depend upon the nature of the solid polyolefin as well as

upon the specific characteristics of the liquid hydrocarbon chosen. Suffice to say, one skilled in the art in possession of this disclosure, having studied the same, now has given to him the concept that it is possible to obtain solid products containing substantial quantities of liquid hydrocarbons or fuels by combining such hydrocarbons or fuels with normally solid polyolefin, as herein described.

According to the invention, normally solid high molecular weight polymers that can be employed include polymers of 1-olefins having from 2 to 8 carbon atoms per molecule. The term "polymer of 1-olefin" include homopolymers of 1-olefins having from 2 to 8 carbon atoms and copolymers of these 1-olefins with each other. Representative examples of suitable 1-olefins include ethylene, propylene, butene-1, pentene-1, hexene-1, heptene-1, 4-methylpentene-1, 5-methylhexene-1, 4,4-dimethylhexene-1, 4-ethylhexene-1, octene-1 and the like. Suitable olefin polymers include variously polymerized ethylenes as well as polypropylene. The preferred polymers are ethylene polymers having a density ranging from 0.93 to 1.00, preferably 0.94 to 0.98. The term "ethylene polymers" includes homopolymers of ethylene as well as copolymers of ethylene with minor amounts of higher molecular weight monomers copolymerizable therewith such as propylene, 1-butene, 1-hexene, butadiene, isoprene, and the like. The more preferred polymers are polyethylene and particularly polyethylene having an average molecular weight greater than about 100,000 (as determined from viscosity).

The preferred ethylene polymers as described herein can be prepared according to the method described and claimed in Patent No. 2,825,721 to Hogan and Banks. However, the polymers applicable according to the invention can be prepared by any known method so long as the polymers have the above described properties. The ethylene polymers can be prepared by any of the known solution processes as well as the "particle form" process. (Polymerization of 1-olefins is carried out in suspension and below temperature at which any substantial portion of the polymer formed is in solution in the suspending medium.) The "particle form" ethylene polymers ordinarily have an inherent viscosity ranging from 3-10 and a high load melt index (ASTM D-1238-57T, Procedure F) ranging from 0.6-10.0.

The solid compositions of the invention can be prepared from normally liquid hydrocarbons or hydrocarbon mixtures or fuels which boil from about 100° F. to about 900° F. and higher. Hydrocarbons that can be employed include saturated and unsaturated acyclic, saturated and unsaturated cyclic, and aromatic hydrocarbons or combinations or mixtures thereof. Paraffinic materials including hexanes, octanes, decanes, pentadecanes and the like as well as mixtures of these materials are preferred when smokelessness is particularly desirable. Petroleum refinery hydrocarbon fractions such as gasolines, kerosenes, stove oils, furnace oils, gas oils, cycle oils, diesel fuels, crude oils, topped crude, and the like are especially useful in the invention. Hydrocarbon fractions having flash points ranging from atmospheric to about 200° F. are usually preferred. As is well known by those skilled in the art, the flash point of materials flashing above about 175° F. is determined by the Cleveland Open Cup Method, ASTM D-92-57, and those flashing below 175° F. by the Tag Closed Cup Method, ASTM D-56-56. As indicated above, preferred hydrocarbons are those paraffins or largely paraffinic mixtures or isoparaffinic mixtures which boil between about 200° and about 700° F. Still more preferred are those that boil between about 300° and about 500° F. The preferred components or fractions are more convenient in that the preparation of the solid composition can be effected without the necessity for pressure vessels for the heating step.

The products of this invention sometimes tend slowly to lose the more volatile hydrocarbon component by simple evaporation. This is an advantage in situations

in which it is desired to recover a substantially pure vapor by slow evaporation, which can be aided somewhat and, therefore, controlled as to its rate, by gently heating the composition. When desired to avoid all or substantially all loss by evaporation such as in storage, the product can be stored in a vapor-proof container or wrapping, e.g., aluminum foil, polyvinyl chloride, cellulose acetate, cellophane, Mylar (saturated polyester film), Saran (polymer of vinylidene chloride), polyvinyl alcohol, rigid polystyrene, metal cans, glass jars, bottles, and the like, capable of withstanding pressures which may be reached under the conditions of storage. Further, application of a thin coating of a substantially nonporous resinous or plastic solid material to the solidified hydrocarbon product which effectively seals the same and prevents substantially all loss of volatiles through evaporation can be employed. Coatings which are satisfactory for the purpose are commercial cellulose acetate-butyrate resins dissolved in a xylene-ketone solvent for purposes of application of the coating. Other coating materials that can be employed include cellulose nitrate type lacquers, melamine base resins, alkyd resins, phenolic coatings, carboxymethylcellulose, thermosetting resins, such as phenol formaldehyde resins, and the like.

The utility of such solidified hydrocarbon compositions is readily apparent. The resulting solids can be used as a convenient solid fuel, being thoroughly and efficiently consumed in the process. Such solidified fuel in the form of briquets might be used in conjunction with the conventional charcoal briquets as a "fire starter" for the popular backyard barbecue and outdoor cookery purposes, fireplace logs, and the like.

As an auxiliary ignition or combustion aid in charcoal fires, a preferred hydrocarbon for the solid composition is a paraffinic mixture which contains some light ends for easy starting and rapid burning with either little oxygen or with heavy winds. It should also contain a full range of heavier boiling materials for heat and relatively smoke-free burning. A commercial paraffinic hydrocarbon fuel boiling from about 443 to about 556° F. appears particularly suitable in this respect. It has also been found convenient to use paraffinic hydrocarbons of C<sub>16</sub> or higher with boiling points greater than about 520° F. if smokelessness is particularly desirable. Briquets of n-cetane and polyethylene were found to be virtually smoke-free during combustion.

Another possible use is as a means for storing and transporting selected hydrocarbons. The solidified fuel acts as its own storage vessel and shipping container. When required, the hydrocarbon may be recovered in its original liquid form by merely breaking open or otherwise pulverizing the solid form and simply squeezing out the hydrocarbon. The application of heat and/or vacuum to distill out the volatiles may also be used.

As a further feature of the present invention, the solidified fuel can be stored either above ground, underground, or under water. Indeed, the mass may be shipped or transported by towing over water or submerged under the surface of water. When thus transporting the mass, it is, in some instances, advantageously covered with an impervious coating to act as a sealer to avoid substantially all loss of hydrocarbon.

In the exercise of this present invention, the hydrocarbon and polymer are brought together in a common vessel and blended at a temperature which is approximately 10-60° C. above the melting point of the polymer. If this temperature is above the atmospheric boiling point of the hydrocarbon, the operation is carried out in a pressurized vessel to maintain the liquid state. This blending operation is carried out until the contents of the vessel are completely homogeneous as indicated by its physical appearance. As little as two minutes may be sufficient or as long as 24 hours may be required depending on the temperature and properties of the components. In no case however, should the time or temperature of heat-

ing to be so excessive as to cause deterioration of the polymer or production of a product with too high of an impact penetration value. Undermixing usually results in a product that phase separates upon cooling. The mixing should be conducted for a period of time and temperature such that the composition sets up into a solid product upon cooling, say to room temperature. Ordinarily, for ethylene polymers, a mixing temperature of 260–310° F. and mixing time of 5–15 minutes are satisfactory.

When the product has cooled and solidified sufficiently, a coating or sealer may be applied. The coating may be conveniently applied by dipping but may also be applied by spraying, brushing, or other means.

It is within the scope of the invention to add coloring material during blending to assist in determining the degree of mixing since unblended particles of polymer appear white, and, therefore, can be easily detected. This provides a convenient means for determining when a homogeneous mixture is obtained.

The proportions of hydrocarbon and polymer depend upon the nature of the hydrocarbon and more particularly upon the nature of the polymer. In general, the solidified composition will contain from about 4 to about 40 weight percent of polymer, ordinarily from about 5 to about 20 weight percent polymer. As previously stated, ethylene polymers prepared as in the low pressure process of U.S. Patent No. 2,825,721 are preferred. Such polymers exhibit a density of 0.930 or greater and can be prepared in a variety of molecular weights of up to 300,000 or more. The higher molecular weight types of polymer are prepared under "particle form" conditions (reaction of ethylene over the chromia catalyst in a non-solvent at temperatures below the softening point of the polymer).

It has been found that less ethylene polymer is required than propylene polymer to obtain a solid product, and that less high molecular weight polyethylene is required than low molecular weight polyethylene. For example, compositions containing about 5 weight percent ethylene polymer having an average molecular weight of 290,000 is approximately equivalent to a composition containing about 15 weight percent polyethylene which has an average molecular weight of 90,000. Similarly, when using a low density polyethylene such as that prepared in high pressure processes, more than 25 percent may be required to form the solidified material. Combinations of more than one type of polymer can be used if desired. Small amounts of other solid hydrocarbon materials such as paraffin wax can also be added, if desired. The composition is also receptive to conventional oil soluble dyes and pigments for decorative effects or identification purposes.

The hydrocarbon polymer compositions prepared according to the invention ordinarily have a gross heat of combustion ranging from about 20,000 to about 21,000 B.t.u.'s per pound. Further, the solid or rigid fuel compositions formed according to the invention have an impact penetration less than about 60 percent, preferably less than about 50 percent, and more preferably less than 40 percent, as determined by dropping an impactor having a circular cross-section which is 0.500" in diameter and weighing 141.7 grams from a height of 10" above a surface of the hydrocarbon-polymer composition. Furthermore, the rigid compositions have a compression value less than about 40 percent, preferably less than 30 percent, as determined by a ten-minute, seven pound load test (static test).

Agitation, milling, or other form of mixing during the blending period is generally desirable. However, after the homogenization is complete, the mixture is allowed to cool and solidify without agitation. It is generally desirable to transfer the hot and still fluid product to another more convenient location before solidification

begins where the desired shape of the finished product may be obtained. The solidified hydrocarbon can be cast or molded into pellets, discs, briquets, spheres, cubes, logs, twigs, bars or any shape possible with a hot viscous liquid and in any size depending upon the apparatus available and its capacity for heating, cooling and handling. When desired, the fuel composition can be extruded as rods and cut into discs of suitable sizes for different applications. When a mold is used, it is frequently desirable to preheat the mold in order to prevent premature hardening before the desired shape is attained. The solid product of the invention can be prepared in batch, semi-continuous, or continuous manner.

A better understanding of the invention can be obtained by referring to the following illustrative examples which are not intended, however, to be unduly limitative of the invention.

#### EXAMPLE 1.—PREPARATION OF HYDROCARBON-POLYMER BRIQUETS

A 16.0 g. quantity of particle form high density polyethylene (Polyethylene B) was blended with 75.33 g. Soltrol 170 (isoparaffinic hydrocarbon) in an open vessel at about 150° C. for 3–5 minutes with continuous stirring. The essentially clear hot mixture was then poured into a prepared mold and rapidly cooled to room temperature. A hard, tough, solid composition was formed. The heating value of this fuel was 20,123 B.t.u./lb.

A number of other hydrocarbon-polymer preparations were made. In all cases, the general method of preparation, except for the choice of components, was essentially identical. The hydrocarbon and polymer were blended together at 145–175° C. until the mixture appeared homogeneous, usually in about 2–5 minutes at that temperature. The hot fluid mixture was then cast into a mold of the desired shape, generally spherical.

The materials used in the examples are further described as follows:

**Polyethylene A:** A commercial medium molecular weight polymer (about 90,000 based on inherent viscosity) with a density of 0.96 and a melt index of about 4.0. The polymer was in the form of a fluffy fibrous solid as obtained from a low pressure polymerization process using a chromia containing catalyst.

**Polyethylene B:** A high molecular weight (about 290,000 based on inherent viscosity) polymer with an inherent viscosity of 4.76 and a melt index (high load) of about 1.06. This polymer was in the form of a granular solid obtained by a particle form process in a low pressure polymerization process over a chromia containing catalyst. The particle form process is a process in which polymerization of 1-olefins is carried out in suspension and below temperature at which any substantial portion of the polymer formed is in solution in the suspending medium.

**Polypropylene:** A polypropylene having a density of about 0.90 g./cc. and an average molecular weight of about 40,000.

**Soltrol 170:** A commercial isoparaffinic hydrocarbon fraction with a boiling range of 420–475° F. The aromatic content is nil and the specific gravity is about 0.775.

**Soltrol 130:** A commercial isoparaffinic hydrocarbon fraction boiling between 335 and 410° F. The specific gravity is about 0.755.

**No. 2 fuel oil:** The conventional liquid hydrocarbon domestic fuel familiar in the art, essentially paraffinic and boiling between 450 and 675° F.

The results of the hydrocarbon-polymer preparations are recorded in Table I. The briquets obtained in all runs were solids.

Table I.—Preparation of hydrocarbon-polymer briquets (Example I)

Run No.	Polymer	Hydrocarbon	Percent Polymer	Percent Other	Remarks
1	Polyethylene B	Soltrol 170	9.60		Solid briquet obtained.
2	do.	do.	17.5		Tough solid briquet obtained (20,123 B.t.u./lb.).
3	Polyethylene A	do.	15.0		Hard briquet obtained.
4	A+B	do.	{6.1 A 2.4 B}		Fairly hard briquet obtained.
5	A+B	do.	{6.2 A 1.2 B}		Do.
6	Polyethylene A	do.	14.5	2.2 paraffin wax	Very good briquets.
7	Polyethylene B	do.	4.5		Good briquets (slightly rubbery).
8	Polyethylene A	No. 2 Fuel Oil	15.0		Good briquets.
9	do.	Soltrol 170	13.0	2.0 paraffin wax	Do.
10	A+B	do.	{2.4 A 4.2 B}		Solid briquets.
11	A+B	do.	{2.2 A 3.3 B}	1.1 paraffin wax	Do.
12	Polypropylene	Soltrol 130	15.0		Smooth briquet, slightly rubbery.

## EXAMPLE II.—COATING OF HYDROCARBON-POLYMER BRIQUETS

A number of hydrocarbon-polymer briquets prepared in Example I were sealed with an organic coating to reduce the evaporation of the hydrocarbon component when exposed to atmospheric conditions.

Briquets from Runs 3, 6 and 7 of Example I (Table I) were dip-coated with a solution of cellulose acetate-butyrate resin (Eastman EAR-381-1). This resin has a 13.0 percent acetyl content, a 37.0 percent butyryl content, and an intrinsic viscosity (acetone-ester basis) of 0.90. The resin is dissolved in a 1 : 1 xylene-methyl isobutyl ketone mixture to a solids content of 20 percent. The dipping was carried out at room temperature and the dipped briquets were dried about 6 hours also at room temperature. Film thickness varied from 4 to 10 mils as shown in Table II. The coated briquet was then weighed periodically during exposure to room conditions to test the effectiveness of the seal. The results of these experiments are recorded in Table II.

a petroleum alkylate having an initial boiling point of 352° F. and a density of 0.764 (23° C.). The ethylene polymer was an ethylene-butene-1 copolymer ("particle form," high molecular weight) having a density of 0.944 and a melt index of 1.75 (high load). The blends were prepared by mixing continuously at a temperature ranging from about 240 to about 310° F. for about 10 minutes. The mixing apparatus employed comprised an 1100 ml. stainless beaker provided with an impeller blade driven by a 1/3 H.P., variable speed motor. The beaker was immersed in a constant temperature oil bath. The clear hot dispersion obtained in each run was then poured into a mold and cooled to room temperature. A rigid fuel composition of the desired configuration (usually discs and spheres) was obtained in all runs except Run I. The results of these runs are presented in Table III below.

Table II.—Coating of hydrocarbon-polymer briquets (Example II)

Briquet Source	Trial A		Trial B		Trial C			Trial D	
	Ex. 1	Run 6	Ex. 1	Run 3	Ex. 1	Run 7		Ex. 1	Run 3
Coating thickness (mils)	None	6	None	6	None	4	10	None	16
Briquet diameter (cm.)	2.72	2.76	2.29	2.85	1.70	2.65	2.72	1.30	4.75
Initial weight after drying (g.)	10.15	9.34	7.06	11.87	9.21	11.73	9.12	13.55	48.00
Weight after 1 day	9.85	9.15	6.82	11.62	8.90	11.45	8.92	12.55	47.24
Weight after 7 days	7.02	8.15	4.69	<sup>2</sup> 10.10	6.24	10.10	8.47	10.53	46.95
Weight after 14 days	4.89	7.74	3.31	9.29	4.24	9.34	8.36		
Weight after 21 days	3.81	7.56	2.64	8.86	2.86	8.79	8.32		
Weight after 28 days	3.24	7.42	2.24	8.49	2.01	8.36	8.29	<sup>3</sup> 4.06	<sup>3</sup> 46.40

<sup>1</sup> Approximate. <sup>2</sup> Film cracked on 2d day. <sup>3</sup> After 40 days.

## EXAMPLE III

Spherical briquets of 1 in. diameter weighing 5.2 grams and containing 92.5 weight percent of a petroleum alkylate boiling between 300 and 475° F. and 7.5 weight percent of particle form ethylene-butene copolymer were found satisfactory in lighting conventional charcoal briquet fires. A single 1 in. diameter briquet was sufficient to light a satisfactorily stacked charcoal fire. The effectiveness of this method compared favorably to a method using about 125 ml. of a commercial liquid (charcoal-lighter) with the added advantage that the solid composition was more convenient and produced far less objectionable odor.

## EXAMPLE IV

In another series of runs, a high molecular weight ethylene polymer was blended in varying proportions with

Table III

	Run No.					
	1	2	3	4	5	6
Polymer, wt. percent	2.5	5.0	6.7	8.0	10.0	15.0
Hydrocarbon, wt. percent	97.5	95.0	93.3	92.0	90.0	85.0
Initial melt temp., ° F.	240	240	260	246	250	249
Final melt temp., ° F.	247	263	284	278	287	300
Impact penetration, percent	100	38.8	28.3	5.9	6.4	2.7
10 min., 7 lb. load test:						
Compression, percent	83	36.9	28.0	5.7	5.6	3.8
Wt. loss, percent		32.4	24.8	2.4	2.4	1.0

It can be seen from the above table that a solid fuel product having an impact penetration less than 40% and a compression value less than about 40% can be obtained using as little as about 5 weight percent polymer. Shaped articles having an impact penetration less than

about 40 percent are satisfactory for commercial use. Run 1 resulted in an unsatisfactory product using 2.5 weight percent polymer.

**EXAMPLE IV**

In a further series of runs, the ethylene polymer of Example IV was blended with different hydrocarbon fraction according to the procedure of Example IV and formed into solid fuel compositions. The blend in all runs contained 8 weight percent polymer and 92 weight percent hydrocarbon. The results of these runs are set forth in Table IV.

It can be seen from the above table that satisfactory solid fuel articles can be prepared from high pressure conventional polyethylenes at the higher concentrations of the polymer.

In the preceding examples, the impact penetration value, compression value and weight loss were determined according to the procedures set forth below.

**I. IMPACT TEST**

(A) Sample requirement: Standard sample is a cylinder 1¼" in diameter by 0.580" thick with a tolerance on thickness of plus or minus 0.03". Must meet definition

Table IV

	Run No.						
	7	8	9	10	11	12	13
	Hydrocarbon Type						
	HF Alkylate #1	HF Alkylate #2	Soltrol 170	Base Oil #1	Paraffin Motor Oil Basestock	Naphthenic Motor Oil	Near East Crude
Initial Melt Temp., ° F.....	246	245	248	245	245	245	245
Final Melt Temp., ° F.....	278	285	278	275	295	300	294
Impact Penetration, Percent.....	5.9	8.6	7.2	6.0	6.3	4.5	7.9
10 Min., 7 lb. load test:							
Compression, Percent.....	5.7	5.5	10.5	3.7	2.5	2.3	17.9
Wt. Loss, Percent.....	2.4	3.3	6.8	2.2	0.3	0.8	6.9

The properties of the hydrocarbons employed in the above runs are set forth below.

in all respects. The sample must be free of voids and faces of cylinder parallel.

Table V

	Run No.						
	7	8	9	10	11	12	13
	Hydrocarbon Type						
	HF Alkylate #1	HF Alkylate #2	Soltrol 170	Base Oil #1	Paraffin Motor Oil	Naphthenic Motor Oil	Near East Crude *
API Gravity (60° F.)....	52.7	52.8	51.2	53.0	33.1	29.6	-----
Flash Point, ° F.....	132	129	185	145	-----	-----	-----
I.B.P. ....	352	347	424	357	650	501	375
5%.....	358	352	-----	-----	680	610	-----
10%.....	360	357	429	-----	689	616	-----
20%.....	365	369	432	-----	697	626	-----
40%.....	376	376	-----	-----	710	636	-----
50%.....	381	381	437	390	715	646	-----
90%.....	497	470	448	472	749	690	-----
E.P. ....	567	567	460	549	771	725	-----

\* Light ends cut to 375° F.

**EXAMPLE VI**

In another series of runs, two different polyethylenes (linear low pressure and conventional high pressure) in varying amounts were blended with an HF alkylate according to the procedure employed in the previous examples and then molded into rigid fuel articles of the desired configuration. The results of these runs are set forth in the table below.

(B) Scheduling of test: Run test on the first day following sample preparation at the earliest, but not later than the third day following preparation at the latest.

(C) Conditions: Ambient.

(D) Procedure:

- i. Place sample in impact machine.
- ii. Drop impactor and measure depth of penetration.

(E) Specifications: Impactor weighs 141.7 grs. and is

Table VI

Run No.....	14	15	16	17	18	19
Polyethylene Type.....	Low Pressure	Low Pressure	Low Pressure	Conv. Hi Pressure	Conv. Hi Pressure	Conv. Hi Pressure
Density.....	0.950	0.950	0.950	0.914	0.915	0.921
Melt Index.....	4.0	6.5	1.2	7.8	3.1	0.15
Polyethylene, Wt. percent.....	20.0	30.0	40.0	20.0	30.0	40.0
Hydrocarbon, Wt. percent.....	80.0	70.0	60.0	80.0	70.0	60.0
Impact penetration, percent.....	4.4	1.1	1	53.3	2.4	1.5
10 Min., 7 lb. load test:						
Compression, percent.....	2.5	2.0	1	14.9	3.2	1.5
Wt. loss, percent.....	1	1	1	9.0	1	1

dropped from a height of 10.0 inches above the top surface of the pellet. Impactor has a circular cross section 0.500" in diameter and presents a flat surface to the sample pellet.

#### II. SEVEN POUND LOAD TEST

- (A) Sample requirement: Standard sample. Must meet definition in all respects.
- (B) Scheduling of test: Run test on the first day following sample preparation at the earliest, but not later than the third following preparation at the latest.
- (C) Conditions: Ambient.
- (D) Procedure:
- i. Blot standard sample lightly with adsorbent paper towel to remove excess surface moisture.
  - ii. Weigh standard sample.
  - iii. Place in 7 lb. load machine and measure initial height; the 5 minute height and the 10 minute height.
  - iv. At the end of 10 minutes blot sample with adsorbent paper, remove the load and reweigh the sample.

The molecular weights mentioned herein are weight average molecular weights and were calculated according to the equation

$$M = \frac{4.03 \times 10^2 \times N_1 \times 14}{2.303} = 24,500 N_1$$

wherein  $M$  is the weight average molecular weight and  $N_1$  is the inherent viscosity as determined for a solution of 0.2 gram of the polymer in 50 cc. of tetralin at 130° C. This type of molecular weight determination is described by Kemp and Peters, *Ind. Eng. Chem.* 35, 1108 (1943), and by Dienes and Klemm, *J. Applied Phys.*, 17, 458 (June 1946).

As will be evident to those skilled in the art, many variations and modifications of this invention can be practiced in view of the foregoing disclosure. Such variations and modifications are clearly believed to come within the spirit and scope of the invention.

#### I claim:

1. Shaped fuel compositions of normally solid polymers selected from the group consisting of polyethylene and copolymers of ethylene and monomers copolymerizable therewith having 3 to 8 carbon atoms per molecule containing 60-96 weight percent of a normally liquid hydrocarbon boiling above 100° F., said composition having an impact penetration less than about 60 percent as determined by dropping an impactor having a circular cross-section which is 0.500 inch in diameter and weighing 141.7 grams from a height of 10 inches above a surface of the composition.

2. A composition according to claim 1 wherein said composition is encapsulated within a material which is substantially impervious to hydrocarbon flow there-through.

3. A composition according to claim 1 wherein said normally solid polymer is an ethylene homopolymer.

4. A composition according to claim 1 wherein said normally solid polymer is a solid high molecular weight ethylene-butene-1 copolymer.

5. A composition according to claim 1 wherein said normally solid polymer is a high molecular weight polymer having an inherent viscosity ranging from 3-10, a high load melt index ranging from 0.6-10, and is present in said composition in an amount ranging from 5-15

weight percent, and wherein said composition has an impact penetration less than about 40 percent.

6. A method for forming shaped fuel articles which comprises: blending together 5-20 weight percent of a normally solid polymer selected from the group consisting of polyethylene and copolymers of ethylene and monomers copolymerizable therewith having 3 to 8 carbon atoms per molecule and 95-80 percent of a normally liquid hydrocarbon boiling within the range of 300-900° F. at a temperature above the melting point of the polymer, working said blend at said temperature for a period of time sufficient to form a uniform dispersion, which dispersion upon cooling forms a rigid composition having an impact penetration less than about 50 percent as determined by dropping an impactor having a circular cross-section of 0.500 inch in diameter and weighing 141.7 grams from a height of 10 inches above a surface of the composition, cooling said dispersion below the melting temperature of said polymer, forming said dispersion into a shaped fuel article consisting essentially of said polymer and said hydrocarbon, confining said fuel article within a material that is substantially impervious to hydrocarbon and vapor flow therethrough, and recovering said shaped fuel article.

7. A method for preparing shaped solid combustible compositions which comprises blending together 4-40 weight percent of a normally solid olefin polymer selected from the group consisting of polyethylene and copolymers of ethylene and monomers copolymerizable therewith having 3 to 8 carbon atoms per molecule and 96-60 weight percent of a liquid hydrocarbon boiling above about 300° F. and mixing at a temperature and for a period of time such that an essentially clear pourable liquid is obtained, and then cooling the liquid to obtain said solid composition as a product of the method, said composition having an impact penetration less than about 60 percent as determined by dropping an impactor having a circular cross-section 0.500 inch in diameter and weighing 141.7 grams from a height of 10 inches above a surface of the composition.

8. A method according to claim 7 wherein said blending is carried out at a temperature ranging from about 10 to about 60° C. above the melting point of the polymer and the time of blending ranges from about 5 to about 20 minutes.

9. A method according to claim 7 wherein a coloring material is employed during blending so that the degree of mixing during blending can be observed and checked so that mixing of the blend can be stopped when a uniform dispersion is obtained, and wherein the composition is cooled in a mold to form the fuel composition into the desired geometrical configuration.

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