United States Patent

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[54] **SOLID FIRE LIGHTING FUEL AND PROCESS OF PREPARATION**
11 Claims, No Drawings

[52] **U.S. Cl.** ..... **44/7 D,** 44/21
[51] **Int. Cl.** **C10l 7/02**
[50] **Field of Search** 44/7, 10, 21

[56] **References Cited**

FOREIGN PATENTS

945,439	12/1963	Great Britain	44/7
962,678	7/1964	Great Britain	44/7

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ABSTRACT: A solid fuel briquet, useful for igniting wood in a fireplace or for igniting charcoal or charcoal briquets in outdoor barbecue apparatus and the like comprises a major proportion of a liquid hydrocarbon fuel such as a petroleum distillate fuel, and a minor solidifying proportion of a urea-formaldehyde resin. To prepare the fuel composition, a mixture of a urea-formaldehyde resin syrup and an aqueous emulsion of hydrocarbon fuel is first prepared, and the resin syrup is caused to gel with an acidic gelling agent. By causing gelation while the mixture is in a suitable mold a briquet of desired size and shape can be produced.

SOLID FIRE LIGHTING FUEL AND PROCESS OF PREPARATION

DESCRIPTION OF THE INVENTION

This invention relates to a solid fuel product and its method of preparation. More particularly, the invention concerns the preparation of a solid hydrocarbon fuel in the form of a briquet or similar configuration that can be used for igniting a fire, such as a wood fire in a fireplace in the home or a charcoal fire in an outdoor grill or "barbecue." The fuel is prepared from a liquid hydrocarbon and a solidifying material comprising a urea-formaldehyde resin, the product being formed into a desired shape upon solidification. The final product is white, attractive in appearance, clean in use, easy to handle without elaborate packaging, and ignites readily.

There is considerable demand for a fire-starting material for home use that will present a minimum hazard and yet be effective for its intended purpose. One of the prime uses for a fire-starter is in connection with an outdoor grill using charcoal or charcoal briquets. Most frequently such fires are started with a liquid hydrocarbon fuel, which presents a fire hazard of appreciably magnitude. The home owner also frequently has difficulty in igniting a fire indoors in his fireplace but here of course the use of a liquid fuel is definitely not recommended. Manufactured solid fuels for lighting fires have heretofore consisted either of some form of wax candle or else wood, fiber board, or paper or the like impregnated with paraffin wax. In accordance with the present invention a solidified fuel is provided which furnishes the advantages of a liquid hydrocarbon fire-starter and at the same time minimizes handling hazards.

The prior art contains many disclosures of the preparation of solidified liquid fuels. These include, among others, the familiar napalm gels as well as encapsulated fuels wherein gasoline or kerosene is contained within a three-dimensional polymer matrix.

In accordance with the present invention, a liquid hydrocarbon fuel is solidified with a urea-formaldehyde resin. Although solid fuels of this type are well known in the art, the methods of solidifying the urea-formaldehyde resin vary quite widely and this represents one of the most critical areas in the preparation of a solidified fuel using such a resin or binder. One of the early disclosures relating to solid fuels prepared from a liquid hydrocarbon and a urea-formaldehyde resin is British Pat. No. 589,594 of Shackleton. The teaching in this reference is that an emulsion is made consisting of the liquid hydrocarbon fuel, urea, formaldehyde, ammonium thiocyanate, soluble casein, a wetting agent or dispersant, and water. All of the ingredients except the liquid hydrocarbon are first mixed together and the liquid fuel is then stirred in by means of a stirrer or other emulsifying device to form a soft, stiff, semitransparent emulsion which hardens within 2 to 3 hours. Substitutes for the casein include: glue, albumen and gelatin. A representative emulsifier is a mixture of sodium lauryl sulfonate and the triethanol amine salt of a sulfonated coconut oil fraction containing about 50 percent of lauric acid. In addition to urea-formaldehyde, other resins that are taught by Shackleton include resorcinol-formaldehyde, urea-acetaldehyde-formaldehyde, and urea furfural. However, all of the Shackleton formulations require a considerable period of time for hardening, in some cases as much as 24 hours. Such long setting times do not lend themselves to practical commercial production of solid fuel.

The present invention provides a procedure wherein a solid fuel of the desired type is obtained quite rapidly, gelation occurring within 30 seconds, and complete hardening being obtained in about 30 minutes. Briefly this procedure consists in adding liquid hydrocarbon fuel to a solution of a suitable emulsifier in water which produces a viscous oil-in-water emulsion, then urea-formaldehyde resin syrup is mixed with this emulsion to produce an even more viscous mixture. The final step involves rapid conversion of the urea-formaldehyde resin to the solid state in the presence of an oxy acid of phosphorus, preferably phosphoric acid or phosphorous acid,

which brings about gelation in about 30 seconds. Because of this rapidity of gelation it is necessary to transfer the emulsion to the desired molds within this 30-second period.

While the gelation can be brought about by adding the phosphoric acid after the urea resin syrup has been mixed with the fuel emulsion, there is a preferred alternate procedure which lends itself to continuous operation, wherein the order of addition of the acid of phosphorus and the urea-formaldehyde resin syrup is reversed. Thus in this alternate procedure the acid is added to the emulsion formed from liquid fuel and aqueous solution of emulsifier. While some deemulsification occurs when this is done, the emulsion of hydrocarbon, emulsifier, water, and acid is essentially stable for as long as 48 hours. This alternate procedure removes the difficulty that is inherent in adding a small proportion of acid to a highly viscous mixture.

Listed below are the broad and preferred ranges of proportions for the ingredients that will be used in preparing the solid fuels of this invention:

Component	Weight Percent Concentration	
	Broad	Preferred
Liquid hydrocarbon fuel	70–90	75–88
Urea-formaldehyde resin	3–15	5–12
Emulsifier	0.2–	0.2–2
Water	5–18	5–14
Acid of Phosphorus	0.1–5	0.2–1.5

In the above tabulation the weight percentages for the urea-formaldehyde resin and for the emulsifier are on a dry basis, that is excluding any water that may have been present in these components as purchased. The water in these materials, if any was present, will be included in the total amount of water recited.

The liquid hydrocarbon fuel that is employed in this invention should preferably have a minimum flash point of 105° F. and more preferably of 125° F. Generally, hydrocarbons boiling in the range of from about 250° to about 680° F. will be employed. For best results the minimum initial boiling point will be no lower than about 300° F. and not more than about 25 volume percent should boil above about 560° F.

Table I which follows lists the inspections for five representative liquid fuels that can be used in practicing this invention.

TABLE I

	Fuel A	Fuel B	Fuel C	Fuel D	Fuel E
Inspections:					
Gravity, °API	50.8	53.3	47.0	38.6	38.3
Flash point, ° F	105	135	.....	140	.....
ASTM distillation [1]:					
I.B.P., ° F	312	368	246	400	468
5%, ° F	318	370	370	426	518
50%, ° F	322	375	415	469	562
95%, ° F	344	392	474	528	620
F.B.P., ° F	353	395	500	543	635

[1] ASTM Test D-86.

NOTE:
(A)—Also known as Stoddard Solvent (Varsol).
(B)—Predominantly isoparaffinic (over 90% isoparaffins).
(C)—Also known as Refined Oil No. 9.
(D)—Also known as Stove Oil.
(E)—Also known as Mentor 29.

The particular hydrocarbon fuel that is used should be selected on the basis of ease of ignition and burning properties as well as odor. Particularly useful because of satisfactory odor are highly refined and highly isoparaffinic synthetic hydrocarbons that have been obtained by alkylation reactions involving isobutane and olefins from three to five carbon atoms. The alkylate is distilled to secure the product of the desired boiling range. These isoparaffinic fractions will contain at least 50 volume percent of isoparaffins, preferably at least 75 volume percent of isoparaffins. The selected cut of isoparaffins can be hydrofined and then treated with caustic and with adsorbents such as silica gel, alumina, activated char, or a zeolite. Highly isoparaffinic hydrocarbons can also be secured by the hydrogenation of unsaturated branched chain olefins of the appropriate boiling range. A representative isoparaffinic fraction has the following typical inspections:

FUEL F

ASTM D-86 Distillation °F.	IBP	348
	5%	350
	50%	356
	95%	368
	Dry Point	370
	FBP	376
Flash, Tag. C.C., °F.		125
Hydrocarbon types: Vol. %		
Total Isoparaffins	93.8	
1 ring naphthenes	5.9	
2 ring naphthenes	0.1	
Aromatics	0.2	
Kauri Butanol Value	27.3	

The urea-formaldehyde resin syrup that is used in the practice of this invention can have a urea-formaldehyde concentration from about 50 to 90 percent by weight, but preferably the resins solid content is in the range of about 60 to 75 wt. percent. The viscosity of the urea-formaldehyde aqueous syrup can range from about 200 cps. to about 2,000 cps. but it is preferably within the range of about 300 to about 800 cps. In general, the mole ratio of formaldehyde to urea in the urea-formaldehyde composition will be in the range of about 1.4:1 to about 2.8:1. Good results are obtained when the formaldehyde to urea ratio is in the range of from about 1.6:1 to about 2.4:1.

A particularly important feature of this invention is the selection of the emulsifier that is used. The emulsifier should be of the anionic type, as the nonionic and cationic emulsifiers in general do not give satisfactory emulsions. Representative emulsifiers of the anionic type include triethanolamine oleate, glyceryl monostearate and sodium oleate. Particularly useful anionic emulsifiers are the dialkyl esters of alkali metal sulfosuccinic acid, as for example the diethyl, the diamyl, or the dioctyl ester of sodium or potassium sulfosuccinic acid. Such materials are available under the trade names Aerosol GPT, Aerosol AY and Aerosol OT, respectively. The selection of the particular surfactant or emulsifier that is used depends on finding one that will form an emulsion that is stable at high hydrocarbon to water ratios, i.e. as high as 9.5 to 1 and will remain stable during solidification with the urea-formaldehyde resin in the presence of the acidic gelling agent.

The phosphorus acid gelling agent can be any oxy acid of phosphorus, e.g. metaphosphoric, pyrophosphoric, hypophosphorous, etc., but preferably either H_3PO_4 or H_3PO_3, and most preferably H_3PO_4. The amount of gelling agent that is used can be in the range of 0.1 to 5 wt. percent but will usually be in the range of from about 0.2 to about 1.5 wt. percent, based on the entire composition. Orthophosphoric acid is generally obtainable in about 80 to about 90 percent purity.

The nature of this invention and the manner in which it can be practiced can be better understood when reference is made to the following examples which include a preferred embodiment.

EXAMPLE 1

A solution was prepared by dissolving 5 grams of the dioctyl ester of sodium sulfosuccinic acid (Aerosol OT) in 80 milliliters of distilled water. This solution was placed in a 3,000 milliliter vessel fitted with a stirring paddle, then while the solution was stirred there was added 1,000 milliliters of fuel C, identified in table I, in three portions to form a white, stable, semiviscous paste. Then while stirring was continued, 150 grams of urea-formaldehyde resin syrup (Lauxite UF-1018) was added giving a white, stable, viscous mixture. The syrup contained about 35 wt. percent water and 65 wt. percent of urea-formaldehyde resin prepared from about 2.1 moles of formaldehyde per mole of urea. To this mixture there were added 4 ml. of 85 percent orthophosphoric acid and 4 ml. of water with continued mixing. After the acid had been added the mixture was stirred for 30 seconds, then the mixing paddle was removed and the mixture was allowed to stand until hardening had been completed, which took about 30 minutes. The solidified mass was then cut with a knife into blocks which were allowed to stand for a few hours until about 5 to 10 percent of moisture and hydrocarbon had evaporated. This minimized bleeding in subsequent storage when the blocks were packaged. All of the above operations were conducted at ambient temperature, which was about 70° F.

EXAMPLE 2

A solid fuel product was prepared having the following composition:

Ingredients	Composition, wt. %
Aerosol OT	0.5
Water	12.0
Hydrocarbon	77.0
UF Resin (Dry Basis)	10.0
H_3PO_4	0.5

This composition was made in the following manner. The hydrocarbon was a blend of 70 vol. percent of fuel F and 30 vol. percent of fuel E. The emulsifier was mixed with sufficient water to give a 25 percent aqueous solution in a 45 gallon quantity; then while the solution was stirred the hydrocarbon was added at room temperature to form an emulsion. A sufficient quantity of this mixture was transferred to a 5 gallon polyethylene container to make up 2.3 gallons when the water-miscible urea-formaldehyde resin syrup was mixed into the viscous emulsion. The urea-formaldehyde resin syrup was the same as that used in example 1. Thereafter, with stirring, 85 percent orthophosphoric acid solution was added quickly to the 2.3 gallons of viscous mixture and mixing was continued for 5 seconds. At the end of this period the mix was transferred as rapidly as possible to a wooden tray 18 inches wide by 24 inches long by 1½ inches deep. The surface of the mix in the tray was smoothed over, and then a metal grid was placed on top of the tray and pressed into the partially cured solid fuel to mark off the material into the desired size of blocks, in this case the individual blocks being 2¾ inches by 1⅜ inches by 1 inch deep. The grid was then removed after a few minutes and the contents of the tray were inverted onto a heavy wire mesh screen. The product, which was initially rubbery in nature, hardened within 30 minutes. It was then allowed to condition overnight in a well ventilated room. This step was required in order to dry the product to some extent so as to prevent condensation of liquid within the package when the material was subsequently wrapped in a laminate of cellophane and Saran and then packaged in a cardboard carton.

In the above procedure, the emulsion of hydrocarbon, water and emulsifier had a viscosity of 30 poises. After the urea-formaldehyde resin syrup was added the resulting more viscous mixture had a viscosity of 83 poises. This procedure is acceptable for a batch operation, but in view of the relatively high viscosity of the mix after the urea-formaldehyde resin syrup has been added, it is difficult to add the relatively small quantity of phosphoric acid and mix it with a large volume of high viscosity mixture in a continuous operation. Accordingly, an alternate procedure is preferred as shown in example 3

EXAMPLE 3

A fuel product having the composition shown in example 2 was prepared in the following manner. After the hydrocarbon had been emulsified with the emulsifier and water, the phosphoric acid was added to the mixture. This reduced the viscosity to about 3.5 poises. However further demulsification

did not occur over a period of 48 hours. Urea-formaldehyde syrup (Lauxite UF–1018) consisting of 65 wt. percent of urea-formaldehyde on a dry basis and 35 percent of water was added to the emulsion containing the phosphoric acid and the resulting mixture was rapidly transferred to a wooden tray mold and handled as in example 2. The resulting solid fuel samples were found to be equivalent to those prepared by the method of example 2.

EXAMPLE 4

Example 3 is repeated on a continuous basis. An emulsion is prepared consisting of 0.6 wt. percent of Aerosol OT, 9.1 wt. percent of water, 89.5 wt. percent of hydrocarbon and 0.8 wt. percent of orthophosphoric acid. The hydrocarbon is a mixture of equal volumes of fuel B and fuel E of table I. A urea-formaldehyde resin syrup is prepared consisting of 65 wt. percent of urea-formaldehyde resin and 35 percent of water. The acidified emulsion and the urea-formaldehyde resin syrup are fed through separate conduits into an in-line blender in the proportion of 85 volumes of the former to 15 volumes of the latter. The resulting mixture is run into a succession of molds traveling on a conveyor operated at such a rate that as the trays leave the conveyor the final blocks or briquets have sufficiently hardened for further handling. A typical product unit consists of a 20-ounce block about 14½ inches long by 2¾ inches wide and 1⅜ inches high, scored transversely with deep notches so that the block can be easily broken into one dozen briquets.

The in-line blender used in this continuous process comprises a conical mixer in the form of an inverted hollow cone 1½ inches high with a 4-inch diameter base fed by two input lines leading from the separate feed conduits mentioned above. Positioned within the hollow cone is a solid rotating cone of sufficiently smaller size to provide a ¼ inch annulus through which the liquids pass. Teeth mounted on the solid cone extend into the annulus to provide the mixing action. Input pressure in the feed lines is 40 p.s.i.g., the inner cone rotating speed is 400 r.p.m., and the output of material is 49 to 50 pounds per minute.

EXAMPLE 5

Example 1 was repeated, substituting an equivalent amount of phosphorous acid, H_3PO_3, for the orthophosphoric acid. The product obtained was equal in all respects to that of example 1.

Comparative Example A

Example 1 was repeated with the exception that an equivalent volume of formic acid was used in place of phosphoric acid. It was found that the gelling time was increased to 5 minutes and the product remained in a rubbery state even after 2½ hours. Furthermore the product was extremely wet with hydrocarbon, which indicated that the emulsion had not properly solidified.

Comparative Example B

Example 1 was repeated with the exception that oxalic acid, maleic acid, citric acid, and acetic acid, respectively, were substituted for phosphoric acid. Initial hardening, or gelation, occurred after 2 minutes with oxalic and maleic acids, and after 5 minutes with citric acid. However, while the final products seemed to outward appearance to be acceptable materials, they were found to undergo excessive bleeding of hydrocarbon from the pores of the matrix, indicating that satisfactory encapsulation of the hydrocarbon fuel had not been obtained. The same was true of the product made with acetic acid, which was additionally unacceptable because initial hardening required 5 to 6 hours.

Example 1 was again repeated, substituting equivalent amounts of hydrochloric acid and of sulfuric acid, respectively, for the phosphoric acid. Initial hardening in each instance occurred in less than 10 seconds. Such rapid gelation militates against practical use of those acids because it permits essentially no time for transfer of the product into a mold.

Comparative Example C

Following the procedure of example 1, various fuel components were substituted for the fuel used therein, so that their effects on the color and ignition and burning characteristics of the solid fuels thereby prepared could be evaluated. There was no significant difference in gelling time or ease of manufacture when using the various hydrocarbon fractions. The comparative data obtained are given in table II. Ignition was by the simple application of a lighted match.

TABLE II.–CHARACTERISTICS OF VARIOUS SOLID FUEL PREPARATIONS

[Composition, Wt. Percent: Hydrocarbon, 75–78; U–F Resin 9–10.2 (dry basis); Water 12–13.8; Aerosol OT, 0.5; H_3PO_4; 0.6]

	Hydrocarbon fuel [1]			
	Fuel C	Fuel E	Fuel B	Fuel B/fuel E equal volume blend
Product color	White	Off white	White	White.
Ignition properties	Immediate	Slow [2]	Immediate	Immediate.
Burning characteristics:				
Sample weight, g.	20.1	22.3	14.2	11.
Burning time, min.	10	9	8	7.
Burning rate, g./min.	2	[3] 2.5	[4] 1.8	1.6.

[1] See Table I.
[2] Several seconds,
[3] Produced the most smoke. Relatively large amount of oil seepage from sample during burning, leaving an oily residue after flame extinguished.
[4] Best flame noted.

As shown in table II, the product made from fuel E was objectionable in that it was off white in color, was slow in igniting and burned rather poorly leaving an oily residue. This indicates that fuel E alone had too high a boiling range to give a product that would be as acceptable as the products made with the lower-boiling-range fuels. All of the other products ignited readily, burned steadily, and had comparable burning rates of 1.6 to 2 minutes per gram for samples ranging in size from about 11 to 22 grams. The best flame was obtained with the product made from an isoparaffinic fraction, fuel B. For long storage life as well as minimum odor of hydrocarbon and formaldehyde the solid fuel made from a blend of fuel B and fuel E was selected as being the most acceptable.

Storage Test

Using the procedure in Comparative example C, solid fuels were made containing from 75 to 77.5 wt. percent hydrocarbon, 9 to 10.2 wt. percent urea-formaldehyde resin, 12 to 13.8 wt. percent water and 0.6 wt. percent phosphoric acid. The fuels used were fuels A, B, C, D and E of table I. Representative laboratory samples of each of the solid fuel products were subjected to weathering in the open, and in closed metal containers. After 52 days the preparation containing fuel E

retained 90 percent of its original weight. In comparison, after 18 days the sample containing fuel A lost 90 percent of its original weight, meaning that only the nonvolatile urea-formaldehyde polymer matrix had remained. The product containing fuel D lost about 20 percent of its weight in 20 days and the product containing fuel C lost 40 percent of its weight in 24 days. None of the samples lost more thin about from 3.5 to 4.5 percent of their weight after 4 weeks when kept in a closed container.

Samples of solid fuel prepared as in example 2, from a blend of 70 volume percent of fuel B and 30 volume percent of fuel E, these samples having a nominal initial weight of about 20 oz., were wrapped in a thin laminate of cellophane and saran (polyvinylidene chloride) and enclosed in a cardboard box. After 60 days they had lost only 2 percent of their weight. By contrast, a sample that had not been wrapped lost 13 percent of its weight in 25 days.

This solid fuel ignited readily, burned with a steady flame, and was successfully used to light wood in a fireplace as well as charcoal in an outdoor barbecue.

The examples herein presented are by way of illustration and are not intended to limit the scope of the invention, which is defined by the claims appended hereto.

What is claimed is:

1. A process for preparing a solid fuel, which comprises the steps of forming an emulsion of a liquid hydrocarbon, an aqueous solution of an anionic emulsifier, and an oxy acid of phosphorus, and thereafter mixing said emulsion with an aqueous syrup of urea-formaldehyde resin whereby said urea-formaldehyde resin is rapidly converted to a solid state, the proportion of the components used in said process being within the range of from about 70 to about 90 wt. percent of liquid hydrocarbon, from about 3 to 15 wt. percent of urea-formaldehyde resin, from about 0.2 to 5 wt. percent of emulsifier, from about 5 to about 18 wt. percent of water, including the water in said aqueous syrup, and from about 0.1 to 5 wt. percent of said acid, said weight percents being based on the total composition, said liquid hydrocarbon boiling within the range of about 250° to about 680° F.

2. Process as defined by claim 1 wherein the proportions of components are within the range of about 75 to 88 wt. percent of liquid hydrocarbon, from about 5 to 12 wt. percent of urea-formaldehyde resin, from about 0.2 to 2 wt. percent of emulsifier, from about 5 to 14 wt. percent of water, and from about 0.1 to 1 wt. percent of said acid.

3. Process as defined by claim 1 wherein said acid of phosphorus is orthophosphoric acid.

4. Process as defined by claim 1 wherein said acid of phosphorus is phosphorous acid.

5. Process as defined by claim 1 wherein said urea-formaldehyde resin has a mole ration of from about 1.4 to about 2.8 moles of formaldehyde per mole of urea.

6. Process as defined by claim 1 wherein said anionic emulsifier is a dialkyl ester of sodium sulfosuccinic acid.

7. Process as defined by claim 1 wherein said emulsifier is the dioctyl ester of sodium sulfosuccinic acid.

8. A continuous process for the preparation of a shaped solid fuel which comprises the steps of emulsifying a liquid hydrocarbon boiling within the range of about 250° to 680° F. with an aqueous solution of an anionic emulsifier, adding to said emulsion from about 0.2 to about 1.5 wt. percent of oxy acid of phosphorus, continuously blending a flowing stream of the resulting acidified emulsion with a flowing steam of an aqueous solution of urea-formaldehyde syrup, and flowing said blended streams into a moving succession of molds, wherein said blended streams are rapidly converted into a solid material as a result of contact of said acid with said urea-formaldehyde syrup.

9. A solid fuel briquet made by the process defined by claim 1.

10. A solid fuel briquet made by the process defined by claim 1 wherein said hydrocarbon is a hydrocarbon fraction having an initial boiling point of at least about 300° F. and having not more than about 25 volume percent boiling above about 560° F.

11. A solid fuel briquet made by the process of claim 1 wherein said liquid hydrocarbon is at least 50 volume percent isoparaffinic.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,615,286 Dated October 26, 1971

Inventor(s) Ronald C. Vander Linden

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 2, in the table embraced by lines 20-28, in the column labeled Broad, opposite the word "Emulsifier", change "0.2-" to read -- 0.2-5 -- . In column 8, line 12, change "ration" to -- ratio -- .

Signed and sealed this 29th day of May 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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