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COMPRESSED FUEL UNITS OF
DIISOPROPYLIDENEGLYOXAL

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This invention relates to combustible materials and more particularly to small units of a solid concentrated source of heat which are useful for heating small quantities of food or for kindling fires. Such units are particularly valuable to campers, picnickers and troops in the field.

Objects and advantages of the invention will be set forth in part hereinafter and in part will be obvious herefrom, or may be learned by practice with the invention, the same being realized and attained by means of the processes, steps, and combinations pointed out in the appended claims.

The invention consists in the novel steps, processes, combinations and improvements herein shown and described.

Various materials have been suggested and used for this general purpose in the past. They all, however, have disadvantages of varying degrees.

Solidified alcohols, such as the familiar Sterno, have been used, but these require packaging in heavy cans because they are not true solids but soft gels usually containing some liquid. Consequently, their efficiency in terms of heat delivered per unit weight of package is severely impaired. Further, if the can is allowed to stand open at room temperature, volatilization of the alcohol occurs quite rapidly; for example, up to 55% loss in weight in 19 hours.

Combustible solid waxes have been used but these have a high luminosity, an obvious military disadvantage, and they soften and flow at elevated temperatures. They are quite difficult to ignite and, therefore, usually require a wick or a fuse and they usually produce acrid odors and deposit a considerable amount of soot.

Hexamethylene tetramine has been used and was produced commercially under the trademark "Heatab," and was also used by the military forces of Germany, England, and other nations. This compound, however, is known to produce highly toxic nitrogen containing fumes during burning. It is very soluble in water and it has been found that, when it is stored for a month at 150° F., it has lost over 25% in weight by sublimation.

Metaldehyde deposits considerable soot and produces irritating fumes when burned. On storage for a month at 150° F. it loses almost 30% of its weight. Paraformaldehyde is soluble in water and is completely volatilized after four days of storage at 150° F. When burned it produces a very unpleasant and irritating odor.

Trioxane is soluble in water. Its rate of sublimation (complete volatilization in two days at room temperature) is so high that it must be packed in elaborate and expensive foil sealed packages. The obnoxious odor of formaldehyde is often noticed during burning.

All these materials fall short of the require-

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ments for an ideal fuel unit of the type herein contemplated. These requirements are as follows:

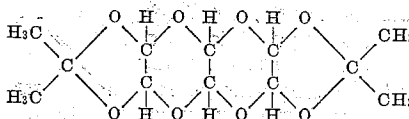
1. Through the temperature range liable to be encountered during storage and shipment (minus 60° F. to plus 150° F.), the fuel units must be chemically stable, remain solid, lose virtually no weight by sublimation, not be affected by water or water vapor, and be resistant to breaking if dropped.

2. From the manufacturing point of view, the fuel must be low in cost, require no heavy or expensive protective packaging, be formed readily into convenient sized tablets by casting, extrusion, cutting or pressing.

3. From the point of view of combustion, the fuel must be capable of ready ignition by a single safety match regardless of the ambient temperature; for example, as low as -65° F. It must burn with a flame that does not deposit a substantial quantity of soot on the surface being heated and must not yield products of combustion which are highly toxic or irritating. It must burn with a wind-resistant flame and, if it is to be used for military purposes, it must burn with a non-luminous flame in order to avoid observation and detection by the enemy. It must deliver enough heat so that a small quantity of fuel, for example, 1/2 ounce is capable of heating an individual portion of food to a palatable temperature. It must burn at a rate which will not burn food, yet fast enough to be practical, and must retain its form or shape during burning and not flow.

An object of the present invention is to provide a composition which overcomes all the disadvantages of the prior art fuels, and which meets every one of the requirements which have been enumerated above for an ideal fuel unit. We have found that diisopropylideneglyoxal, hereinafter referred to as DIPG, when, admixed with a suitable supporting agent, meets every requirement listed above.

DIPG has been synthesized before, but no practical use for it has ever been suggested. Fischer and Taubé report its synthesis in *Berichte* 59:854 (1926). Raudnitz reports the synthesis in *J. Chem. Soc. (London)*, page 763 (1948), and reports a melting point of 207° C. and assigned the following empirical and structural formulae: $C_{12}H_{18}O_8$



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There has been some controversy in the literature over the correct assignation of structure but, for our purposes, it is not necessary to resolve that problem. It is sufficient to know that, using the method of Raudnitz, we have synthesized from glyoxal sulphate and acetone, in an excess of acetone, a compound which has a sharp melting point at 206–7° C. and an analysis as follows:

Calculated for $C_{12}H_{18}O_8$	Analysis
Percent C 49.66 H 6.21	Percent C 49.82, 49.75 H 6.61, 6.53

This compound is a white solid which crystallizes in plate-like form and has a somewhat waxy feel. It is not only insoluble in water but is actually hydrophobic.

The DIPG is admixed with from about 1% to about 15% by weight of a supporting agent, and preferably about 3% by weight of a supporting agent of a cellulosic, carbonaceous or siliceous nature or combination thereof.

Virtually any form of cellulose will act as a supporting agent for DIPG. For convenience of uniform incorporation, it is desirable to use a finely divided cellulose flock. Satisfactory compositions are obtained with fibers having an average length under 2 mm., but this size is not critical. In order to eliminate odor, smoke or residue from the fuel the cellulose must be of high purity. Preferred celluloses have an ash residue of less than 0.5% and are contaminated with less than 0.5% of materials such as lignin, inorganic salts, and the like. A high alpha-cellulose content (about 95%) is desirable.

An example of a particularly useful cellulose is that available commercially under the name "Solka-Floc SW-40A" (Brown Co.). The manufacturer's specifications are that it consists of pure, soft, white, strong, absorbent, finely divided, chemically purified, wood cellulose fibers in an easy-to-handle flock form. The average fiber length is 165 millimicrons. The alpha-cellulose content is 94%, the remaining 6% is substantially beta- and gamma-cellulose and the ash is 0.3%.

The carbonaceous materials to be used as supporting agents are those having a high capacity for absorbing and/or adsorbing liquids. Such carbons are those typified as either having a very small particle size, that is, substantially below 400 millimicrons, and preferably below 100 millimicrons, or having a much larger particle size but characterized by a structure which is highly porous, and in which the pores are relatively large as compared to the particle size.

For convenience in obtaining a uniform mixture with DIPG, it is desirable that the carbon be in a powdered form, rather than in a granular form. Preferably 98% or more of the carbons should pass through a 50-mesh screen.

In the preferred form of carbon powder, it is not sufficient for the ratio of surface to volume to be high. Certain charcoals and activated carbons, which have a high adsorptive capacity for gases, do have a very high surface to volume ratio. These materials, however, are characterized by a structure having very many more pores of very small diameter. Such a structure, which is exhibited by coconut charcoal and numerous commercial products designed for use

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in gas masks, air-conditioning systems, solvent vapor recovery systems and the like, makes the carbon not particularly suitable for use with DIPG.

The most preferred forms of carbon are set forth in the following three groups:

1. Carbon blacks. These materials are also known as gas blacks, natural gas blacks, ebony blacks, jet blacks, hydrocarbon blacks, satin gloss blacks, and silicates of carbon. They are normally the product of incomplete combustion of gas, deposited by contact of the flame on a metallic surface. Structurally, they are considered to be mainly crystalline, blended with some amorphous particles. They are usually hard and brilliant. An example of a useful material in this group is Super Spectra Black (Binney and Smith Co.). It is a high color carbon black pigment with a particle size between 10–20 millimicrons. A sludge of the carbon is reported to have a pH of 5.2. Chemisorption of diphenyl guanidine is reported to be about 3 moles per gram $\times 10^5$. The oil sorption value is reported to be 28. The surface available is reported as over 22 acres per pound; the tinting strength as 99.

2. Acetylene blacks. These materials, formed by the decomposition of acetylene, are not useful either as gas adsorbents or decolorizing agents. Their principal uses are in plastic and rubber compounding, and in making dry cells. An example of a useful material in this group is Shawinigan Acetylene Black (50% compressed) which is made by the thermal decomposition of acetylene. As deduced from X-ray diffraction and electron micrograph studies reported in the literature, the particles are composed of many crystalline zones (micelles or crystallites) in random orientation. The particles are joined together in a chainlike or fibrous fashion so that the mass of the black has a three dimensional "fishnet" structure. The following properties have been reported:

Apparent density	6.25 lb./cu. ft.
Mean particle size	45 millimicrons
Surface area (by various methods)	65–85 sq. m./g.
Absorption capacity	10 ml./g.
Absorption-stiffness value	30
pH	8.0
Purity	over 99.5% carbon

Shawinigan Black will not sustain its own combustion, but will glow if ignited in the presence of substantial amounts of other materials. It is not readily wet with water, but has an extremely high absorption capacity for organic liquids.

3. Vegetable decolorizing carbons. These carbons, which have a larger particle size than the two preceding groups, may be made in many ways. Their effectiveness as supporting agents depend to some extent on the method of manufacture, because porosity and compactness depend on the conditions under which carbonization has been effected. Decolorizing chars made by carbonization of lignite are especially useful; those made by carbonization of paper-mill waste liquors are less effective. All decolorizing carbons are activated after carbonization. They are soft chars which appear as black glistening powders.

An example of a useful material in this group is Darco G-60 (Darco Corp.), which is made by carbonization of lignite, then activated by air and steam. It has a somewhat granular structure

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under the microscope, and is reported to have the following properties:

Carbon	93-96%
Ash	3-6%
HCl-soluble portion	0.20%
pH of water extract	5.6
Density (loose pack)	17.9 lb./cu. ft.
Density (solid pack)	22.5 lb./cu. ft.
Screen analysis (Per cent):	
on 50	1.6
-50, +70	7.9
-70, +100	13.2
-100, +150	16.5
-150, +200	20.3
through 200	40.5

Useful siliceous materials are silicas having 95% or more of the particles with diameters below 40 microns. The preferred silicas are those in which substantially all of the particles have diameters substantially below 10 microns. Two such preferred silicas are aerogel silica and fumed silica. Silicas of high purity (over 90% SiO₂) are desirable. A commercial example of a preferred silica is Linde Silica 30 (Linde Air Products Co.) which is an amorphous fumed silica (99.9% SiO₂), a white powder with a maximum particle diameter of 0.05 micron.

The following examples will serve to illustrate typical embodiments of this invention. In each example an intimate mixture was made of the dry ingredients and this mixture was then formed into pellets by pressing at 6000 p. s. i., at room temperature. The proportions given are parts by weight.

Example 1

Composition:	
DIPG	97
Solka-Floc SW-40A	3

The pellets were smooth and firm. Ignition was easy with a single safety match, even immediately after storing a pellet for several hours in a cabinet kept at sub-zero temperatures with Dry Ice. The pellets burned with substantially non-luminous flames and no smoke. They deposited very little soot on a surface being heated. A half-ounce pellet heated one pound of water from 77° F. to 173° F. in 8.0 minutes. The amount of ash was very small. On storage at 150° F., a pellet had lost only 1% in weight after three weeks.

Example 2

Composition:	
DIPG	97
Super Spectra Black	3

The pellets were very tough and smooth. They ignited easily, burned with a substantially non-luminous flame, and left only a small residue. The pellets retained their shape while burning.

Example 3

Composition:	
DIPG	97
Linde Silica 30	3

This composition formed a good, smooth, firm hard pellet. It ignited readily, burned with a substantially non-luminous flame, did not char or flow during burning.

Example 4

Composition:	
DIPG	97.0
Darco G-60	1.5
Solka-Floc SW-40A	1.5

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The pellets were tough and smooth. They did not shatter when dropped. They could be lit easily with a safety match, and burned with a substantially non-luminous flame. The pellets retained their shape and did not flow during burning.

Example 5

Composition:	
DIPG	97.8
Darco G-60	2.0
Solka-Floc SW-40A	0.2

The pellets were tough and smooth. They were unaffected by immersion in water. They were stable and solid at 150° F. They ignited readily and burned with a substantially non-luminous flame. They showed only slight viscous flow during burning. There was no smoke.

Example 6

Composition:	
DIPG	98
Shawinigan Acetylene Black (50% compression)	2

The pellets were smooth and shiny. They ignited readily and burned with a substantially non-luminous flame. The pellets retained their shape, and showed no flow during burning. There was a minimum of smoke, odor, or unburned residue.

Example 7

Composition:	
DIPG	97.5
Darco G-60	1.5
Shawinigan Acetylene Black (50% compression)	1.0

The pellets were tough, smooth, and shiny. They burned in a manner similar to those of Example 6.

One pellet of this composition was ignited in a wind tunnel, and subjected to gradually increasing air velocity. The flame was not extinguished until the wind had reached a velocity of 25-26 miles per hour.

We have also found that DIPG, with an admixed supporting agent, when compressed, gives a surface which permits coating, for example, by spraying or dipping. This permits us to impart to the fuel tablets certain characteristics which may be desired. For example, it may be desirable to coat the tablets with a flammable, film-forming material such as nitrocellulose for easier low temperature ignition. Such a coating also serves to prevent the carbonaceous type of supporting agent from being deposited on the hands and clothing of the user.

Example 8

After pellets of the composition of Example 7 were molded as usual, they were sprayed over their entire surfaces with a solution having the following composition:

Nitrocellulose (RS grade, 1/2 second viscosity)	5.0
DIPG	1.2
Acetone	25.0
Methyl isobutyl ketone	68.8

When the solvents had evaporated, the coating on an 8-gram tablet weighed 0.04 gram. The pellets had a smooth, polished appearance, and were hard, firm, and non-friable. There was no tendency for carbon to smudge on the fingers when the pellets were handled.

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We found that pellets treated in this manner ignited readily with a paper safety match, even at sub-zero temperatures. The flame spread over the surface more rapidly than in the case of an uncoated pellet. The fuel burned with a substantially non-luminous flame, giving no noticeable odor during burning.

Example 9

Composition:

DIPG	90
Darco G-60	5
Solka-Floc SW-40A	5

The pellets were shiny and slightly friable. They ignited readily and burned with a substantially non-luminous flame. They retained their shape and exhibited no flow during burning. Slight intermittent sparking was noticed during burning. After the fuel was consumed, the small residue glowed and emitted slight smoke and odor.

Example 10

Composition:

DIPG	85
Shawinigan Acetylene Black (50% compression)	15

The pellet was somewhat friable. It was ignited very readily with a safety match. The fuel burned with a substantially non-luminous flame. There was no flow during burning. A certain amount of smoke and odor were emanated during burning. There was a considerable unburned residue.

In most instances, as the percentage of admixed supporting agent is increased, the efficiency of the fuel is decreased, while the smoke and odor are increased. Thus a minimum of supporting agent is desired. On the other hand, as little as 1% of supporting agent permits slight flowing of the fuel and therefore it is preferable to maintain the admixed supporting agent at about 3%.

The invention in its broader aspects is not limited to the specific processes and steps shown and described but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantage.

What is claimed is:

1. A compressed fuel unit comprising diiso-

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propyrideneglyoxal as the major constituent of said fuel unit and from about 1% to about 15% by weight of a supporting agent admixed with said diisopropylideneglyoxal, said supporting agent being substantially non-luminous and substantially non-smoke-producing on combustion of said diisopropylideneglyoxal.

2. The fuel unit of claim 1 wherein the supporting agent is present in an amount of about 3% by weight.

3. The fuel unit of claim 1 in the form of a compressed tablet having a coating of nitrocellulose.

4. A compressed fuel unit comprising diisopropylideneglyoxal as the major constituent of said fuel unit and from about 1% to about 15% by weight of a supporting agent admixed with said diisopropylideneglyoxal, said supporting agent being a member of the group consisting of finely divided solid cellulosic material, solid carbonaceous material having a particle size of less than 400 millimicrons, and finely divided solid decolorizing carbon material.

5. The fuel unit of claim 4 wherein the supporting agent is carbonaceous material having a particle size of less than 400 millimicrons.

6. The fuel unit of claim 4 wherein the supporting agent is a decolorizing carbon.

7. The fuel unit of claim 4 in the form of a compressed tablet having a coating of nitrocellulose.

8. The fuel unit of claim 5, wherein the supporting agent is carbon black.

9. The fuel unit of claim 5, wherein the supporting agent is acetylene black.

10. The fuel unit of claim 4 wherein the supporting agent is cellulosic.

11. The fuel unit of claim 1 wherein the supporting agent is siliceous.

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REFERENCES CITED

The following references are of record in the file of this patent:

- Fischer et al., Chem. Abstracts, vol. 20, p. 2821 (1926).
 Raudnitz, Chem. Abstracts, vol. 42, p. 8162 (1948).