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3,174,838

## FUEL MIXTURES

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This invention relates to artificial or synthetic fuel mixtures comprising a cellulosic carrier and a combustible liquid and characterized by their ease of preparation, safety, and long burning life. The mixtures are of the type which, but for the presence of the carrier, would burn out in a short time; the use of the carrier, however, more than doubles the burning life of the combustible liquid. While capable of broad utility, the mixtures are particularly applicable as cooking fuels of the type sold in non-combustible containers and used therein, and the invention will therefore be particularly described in relation to such fuels.

Packaged cooking fuels are of course quite well known; one of the more conventional of these comprises the so-called solidified alcohols, a fuel comprising a mixture of conventional cellulose nitrate and one or more lower aliphatic alcohols like methanol, ethanol, etc. Such a mixture is usually made by dissolving the cellulose nitrate in the alcohol so that the resulting solution is almost saturated by the cellulose derivative, then precipitating the latter by adding a non-solvent such as water. The precipitated cellulose nitrate is in the form of a gel which holds the liquid portion of the mixture. Invariably the mixture exhibits syneresis or bleeding and does not attain the desired over-all solidified state. The mixture is in fact non-uniform and unattractive. Care is obviously required to dissolve the cellulose nitrate to obtain an almost saturated solution, and similarly, care is required to precipitate the nitrate so as to form a gel which will retain most of the liquid. The manufacturing process is thus a painstaking one, and it does not result in an attractive product, although the appearance of the product as a factor in its sale is lessened by the fact that it is put up and sold in sealed opaque containers; in other respects, however, the bleeding, watery state of the material makes it difficult to transfer it from the container to other points of application when so desired. When the product is ignited, its burning quality is characterized by sputtering, crackling, and sparking.

By contrast, the fuel mixtures of the invention are prepared by simple mixing, are uniform and attractive, safe to use, and burn smoothly and evenly. They are further characterized by being convertible into different forms of utility; thus a mixture initially prepared in the form of a gelatinous mass may be converted into a firm gel, as for use in napalm or other explosives, and may also be converted to a fluid gel or dispersion suitable for dispensing from an aerosol can. Of perhaps even greater importance is the fact that the mixtures are capable of burning for a longer time than the conventional cellulose nitrate-containing fuels having the same combustible liquids.

The invention, briefly, resides in a fuel mixture made from a cellulosic carrier and a combustible liquid wherein the carrier comprises cellulose crystallite aggregates. The aggregates are a non-fibrous, infusible material particularly characterized by having in and on their surfaces a multiplicity of cracks, pores, fissures, voids and the like, by means of which the aggregates are able to retain the liquid or liquids with which they are mixed. The combustible liquid may be a conventional one, including methanol, ethanol, propanol, isopropanol, and other lower aliphatic alcohols, mixtures thereof, and if desired, may contain small amounts of other combustible liquids such

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as acetone, other ketones, ethyl acetate, methyl acetate, and the like. Water may be present in the mixture.

Considering the invention in detail, the aggregates are products obtained from the controlled acid hydrolysis of cellulose, there being formed an acid-soluble portion and an acid insoluble portion. The latter comprises a crystalline residue or remainder which is water washed and recovered, being referred to as cellulose crystallite aggregates. Preparation of the aggregates is described in Patent Number 2,978,446. Briefly, although hydrolysis may be effected by various specific methods, including the use of various acids, a direct method which is free of secondary reactions comprises the treatment of the original cellulosic material with 2.5 normal hydrochloric acid solution for 15 minutes at boiling temperature. Another method comprises a treatment with a 0.5% aqueous hydrochloric acid solution for 1 hour at 250° F. It may be observed that "crystallite," as used herein, is a cluster of longitudinally disposed, closely packed cellulose chains or molecules, and that "aggregates" are clusters of crystallites.

The aggregates suitable for use in the invention are characterized by having an average level-off D.P. of 60 to 375 anhydroglucose units. Preferred sources for making such material include cotton linters, wood pulp having a high alpha-cellulose content, alkali-swollen natural forms of cellulose, of which a preferred source is cellulose that has been mercerized by treatment with 18% caustic soda solution at 20° C. for two hours, regenerated forms of cellulose, including tire and textile yarns, other regenerated cellulose fibers, and cellophane.

In every case the cellulosic source material has a D.P. greater than the level-off D.P. thereof.

If desired, the aggregates may be mechanically disintegrated as by subjecting them, preferably in the presence of an aqueous medium, to attrition in a mill, or to a high speed cutting action, or to the action of high pressures on the order of at least 5,000 or 10,000 p.s.i. Whatever method is used the disintegration is extensive enough so that the resulting disintegrated aggregates are characterized by forming a stable suspension, either a gel or a dispersion, in the aqueous medium in which they are being attrited or in which they may be subsequently dispersed. By a stable suspension is meant one from which the aggregates will not settle out but will remain suspended indefinitely, even for periods measured in terms of weeks or months.

Either before or after mechanical disintegration, the aggregates may be dried.

If desired, the aggregates may be fractionated to obtain fractions of more uniform particle sizes. Fractionation may be accomplished by means of such separation procedures as mechanical sifting, settling in water, or centrifuging, a number of useful fractions being obtainable, including fractions having a particle size of up to 1, 2, 5, 10, 40, 50, 100, etc. microns; also fractions of 10 to 100 microns, or 50 to 100 microns, 50 to 200 microns, 100 to 200 microns, etc.

The aggregates per se are white in color, have a physical appearance similar to starch, and are non-toxic. Their purity is not critical.

Quantitatively, the fuel mixture may broadly comprise 10 to 40 or 45% by weight of the aggregates, 80 to 40% of combustible liquid, 10 to 30% of water, and, preferably, a small amount, usually up to 1 or 2%, of a wetting agent. A typical wetting agent is sodium lauryl sulfonate, but it will be understood that any conventional wetting agent or surfactant may be employed. A more preferred fuel mixture may comprise 15 to 25% by weight of aggregates, 70 to 52% of combustible liquid, 15 to 25% of water, and up to 1% of wetting agent. A suitable cooking fuel mixture is one comprising 20-25% ag-

gregates, 57-53% methanol, 18-25% water, and up to 1% of wetting agent. For igniting charcoal, a suitable fuel mixture may comprise 23% aggregates, 46% naphtha, 30% water, and up to 1% of wetting agent. Another suitable charcoal igniter mixture may have 21% aggregates, 52% of a 50-50 gasoline-kerosene mix, 28% water and up to 1% wetting agent. In any of the foregoing formulations the wetting agent may be omitted, but preferably it is not. Small amounts, say 1 to 5%, of paraffin wax may be added, preferably to the kerosene-containing mixtures to increase the burning life. The wax may suitably be dissolved in the kerosene.

The cooking fuel mixture may be made by simply mixing all of the ingredients together in a conventional mixing device such as a Waring Blendor, Hobart mixer, or other similar apparatus. In the concentrations described, mixing of the batch of ingredients for several minutes will produce mixtures ranging from those that are fluid and flowable to those that are less fluid and stiffer. For example, a fuel mixture containing about 24% aggregates, 57% methanol, 18% water, and up to 1% wetting agent is in the form of a thick, white, gelatinous material which exhibits no syneresis and which is easily transferred as with a spatula. Such a material is readily packed in a can, in which it may be ignited and burned, or if desired it may be smeared over charcoal briquettes and ignited, thus serving as a charcoal lighting aid. By diluting the material with alcohol, water, or alcohol and water, or other combustible liquid, a more fluid mass or slurry may be obtained which is suitable for dispensing from an aerosol can. On the other hand, by increasing the aggregates concentration of the material up to about 35% by weight, a firm gel is produced; above about 35% aggregates a doughy product results, the stiffness of which progressively increases with increasing concentration of aggregates. The gel and the doughy material are suitable for use in explosive compositions, such as those containing nitroglycerin, trinitrotoluene, dynamite, etc., in which compositions the aggregates serve as carrier for the explosive ingredients. Other applications include rocket and missile fuel compositions. It will be understood that the foregoing variations in the product may also be obtained by starting with fuel mixtures containing more or less than 24% of aggregates. In another example, a jelly-like mass containing gasoline was made by first mixing the aggregates with water, then adding a mixture of equal parts of gasoline and kerosene, adding liquid soap as a wetting agent, and mixing the whole thoroughly to form a gel-like mass having the following composition: 23.5% gasoline, 23.5% kerosene, 47% aggregates, 1.4% liquid soap, and 4.7% water. In a test, this mixture caught fire very easily and burned for a considerably longer time than an equal amount of a 50-50 blend of gasoline and kerosene.

As indicated, the fuel mixtures are useful for improving the ease of ignition of a fuel like charcoal. The mixture, in the form of a gelatinous mass or paste, may be applied to the charcoal and readily ignited, and in this way the temperature of the charcoal is quickly raised to the ignition point. Suitably, the mixture may be diluted so that it is in the form of a fluid slurry, rather than a paste, and this slurry, being dispensable from an aerosol can, may simply be squirted on the charcoal. Any suitable pressure-dispensing container may be used, employing conventional propellants such as nitrogen, nitrous oxide, carbon dioxide, dichlorodifluoromethane (Freon), mixtures of the same, etc. These containers, or aerosol dispensers, may have a dispensing orifice of conventional size, and despite the small size of the orifice, the slurry is able to pass through and is aerated to some extent during its passage. An advantage of the aerosol-dispensed slurry for igniting charcoal is the safety element provided by the reduced incidence of flash, owing to the physical form of the fuel mixture. It may be noted in this connection that conventional charcoal lighter

products are usually in liquid form and tend to produce flash when ignited. Another advantage of the slurry is that it is slower burning than a conventional liquid product and therefore has a longer opportunity of igniting the charcoal.

As noted, the aggregates exhibit irregular surface phenomena such as cracks, pores, fissures, voids and like irregularities. By virtue of these, the sorptive capacity, by which is meant the absorptive and/or adsorptive capacity, of the aggregates for liquids is enhanced, and the aggregates are able to retain up to several times their weight of liquid material while still exhibiting the overall appearance of a dry, solid material. Furthermore, the good sorptive capacity of the aggregates for the combustible liquid means that, in cases where the fuel mixture is only partly used at a given time, there will be less loss arising from the volatilization of the liquid from the hot residue immediately after the flame has been extinguished.

Being non-fibrous, the aggregates have a small volume or bulk in relation to their weight, which means that a considerable amount of product can be placed in a container of conventional size; this is in contrast to fibrous carriers which bulk to such a large extent that only a small weight of the same may occupy a very large volume.

The aggregates are infusible and thus are able to pay out or supply retained liquid fuel over a period of time, or as long as the supply lasts, without danger of being melted down. They are themselves combustible and will burn after the liquid fuel is used up, leaving little or no residue. The flame is readily extinguishable.

A further advantage of the aggregates, and of fuel mixtures made from them, is their excellent adherence to surfaces. A fuel mixture slurry, or paste or gel, when applied to charcoal briquettes or other surfaces, adheres tenaciously and thus is in a position to burn as closely as possible to the material to be ignited.

As will be understood, the fuel mixtures of the invention are not only easily prepared, are free from syneresis, and are long and even burning, but also they are easily ignited and free of flash. The physical form of the mixtures is easily varied, and regardless of such form, they adhere very well to surfaces on which they may be placed. They provide economies by virtue of the low bulking power and high sorption capability of the aggregates.

For the reasons described, the aggregates are the preferred carrier. However, other suitable carriers, related to the aggregates, are the insoluble, gel-forming, infusible, combustible derivatives of the aggregates comprising oxidation derivatives, ether derivatives and ester derivatives. They are characterized by having a D.S. (degree of substitution) of less than 0.5, say 0.05 to 0.5, and are essentially topochemical derivatives in that the molecular chains disposed in the surfaces of the aggregates are derivatized rather than all of the chains. They are insoluble in the combustible liquids as well as in water.

Examples of oxidation derivatives are the carboxyl derivatives, including the 6-carboxyl and the 2,3-dicarboxyl derivatives; mixed carboxyl- and aldehyde-containing derivatives; the 2,3-dialdehyde; and the carboxy-alkyl ether derivatives such as the carboxymethyl, carboxyethyl, etc. By converting the carboxyl derivatives to their alkaline salts, either alkali metal or alkaline earth metal, such as the sodium, potassium, lithium, or magnesium salts, other useful carriers are obtained.

Ether derivatives contain —OR groups wherein R is an aliphatic radical having 1 to 12 or more carbon atoms, preferably 1 to 6. Specific aliphatic radicals are the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, isopentyl, hexyl, etc., and including substituted radicals like hydroxyalkyl, cyanoalkyl, halogenated alkyl, alkoxy-alkyl aralkyloxyalkyl, etc. R may also be aralkyl,

which may be considered to be a substituted alkyl or aliphatic radical, and which may include groups such as benzyl, methylbenzyl, phenethyl, phenylpropyl, etc. Also, R may be aryl, such as phenyl, tolyl, xylyl, naphthyl, etc. Other ethers include alkylaminoalkyl ethers wherein the alkyl moieties may have 1 to 6 or more carbon atoms; for example, the diethylaminoethyl and triethylaminoethyl ethers of the aggregates.

Other suitable derivatives are ether-esters, such as the alkyl ethers of various esters of the aggregates, including ethers of the acetate and propionate esters.

The ester derivatives include the nitrate, acetate, propionate, butyrate, mixed acetate-propionate, mixed acetate-butyrate, phthalate, benzoate, formate, laurate, stearate, lactate, naphthenate, oxylate, crotonate, cinnamate, and the like.

Also suitable as carriers are mixtures of the aggregates with one or more of the derivatives as well as mixtures of two or more of the derivatives:

All of the foregoing derivatives may be used as carriers in substantially the same manner as the aggregates. They may be made up into fuel mixtures by simply mixing with the combustible liquid, water, and the wetting agent in the manner described.

A particularly useful derivative is the aggregates nitrate, which is usable at a D.S. in the broader range of 0.05 to 2.5. At a low D.S., say 0.05 to 0.5, the nitrate may be used to form fuel mixtures in the manner described for the aggregates. The derivative is also useful at the higher D.S. range of 0.5 to 2.5, although in this range it tends to be more or less soluble in combustible liquids like methanol and ethanol from which it may be precipitated by the addition of a non-solvent like water. The preparation of a fuel mixture by this method is illustrated in Example 4.

The aggregates derivatives have the general advantages of the aggregates, although in at least some cases they are useful in lower concentrations. Thus, suitable fuel mixtures may contain 3-8% of the derivative, 90-60% of combustible liquid, 10-20% water, and up to 2% of wetting agent; more preferably the mixtures may comprise 4-6% of derivative, 85-75% combustible liquid, 12-16% water, and up to 1% wetting agent.

Over-all, the fuel mixtures of the invention may have 3-45% of carrier, 90-40% combustible liquid, 4-30% water, and up to 2% wetting agent; preferably 4-25% carrier, 85-55% combustible liquid, 10-25% water, and up to 1% wetting agent.

The invention may be further illustrated by the following examples.

#### Example 1

A fuel suitable for use in a cooking container was prepared by dry blending 300 parts by weight of cellulose crystallite aggregates and 6 parts by weight of sodium lauryl sulfonate as wetting agent (Duponol ME) for about 5 minutes in a Hobart mixer, then adding 695 parts of methanol and 220 parts of water, and continuing the mixing for 15 minutes to form a thick, smooth, white, homogeneous-looking gelatinous mass having no trace of syneresis. The fuel was identified as No. 161; on a weight percent basis it had the following composition: 24.5% aggregates, 0.5% wetting agent, 56.9% methanol, and 18.0% water.

The aggregates were obtained from the hydrolysis of Ketchikan sulfite wood pulp with 0.5% aqueous HCl solution for 60 minutes at 250° F. After washing with water they were spray dried. They had an average level-off D.P. of about 220.

The fuel was subjected to a burning test together with a control fuel comprising a commercial material trademarked "Sterno" and believed to comprise conventional nitrocellulose, water, and methanol or ethanol or a mixture of these two alcohols. Determination of the solids content of the commercial fuel showed it to con-

tain 10% solids and the balance liquid. Twenty g. of each fuel were taken for the test, and on this bases, the two fuels contained the following ingredients:

| Control             | G. | No. 161         | G.   |
|---------------------|----|-----------------|------|
| Nitrocellulose..... | 2  | Aggregates..... | 4.9  |
| Liquid.....         | 18 | Liquid.....     | 15.1 |

It will be seen that the control had more liquid than No. 161, and the probability is that it also had more liquid fuel. The liquid portion of the control was believed to comprise methanol, ethanol, and water in unknown proportions; while the liquid portion of No. 161 comprised 11.4 g. methanol, 3.6 g. water, and 0.1 g. wetting agent.

It was noted that while No. 161 was in the form of a thick, white spread, the control was a reddish gel in which syneresis or bleeding had occurred to such an extent that the gel was bathed in liquid. The 20-gram portions were each weighed into aluminum foil cups and ignited, and the time required for complete burning was measured by means of stop watches. The control burned for 9 minutes, 30 seconds, sparked considerably during the last part of the burning period, and left little or no residue. No. 161 burned for 10 minutes, 15 seconds, gave a steady, even flame with no sparks, and left little residue. Both portions burned with the blue flame characteristic of burning methanol or ethanol.

As is apparent, No. 161 burned for approximately an 8% longer time than the control, even though it was believed to contain less liquid fuel than the control; and it also burned more evenly. It was considered that the liquid fuel was better sorbed, i.e., adsorbed and/or absorbed, by the aggregates than by the nitrocellulose. Of interest in this connection was the fact that 11.4 g. of methanol (the amount present in No. 161), when placed per se in a foil cup and burned, required a burning time of only 4 minutes, 59 seconds. Sorbing this amount of methanol in the aggregates, as in No. 161, more than doubled the burning time.

#### Example 2

The work of Example 1 was repeated, the following burning times being obtained:

Control ----- 10 minutes, 29 seconds.  
No. 161 ----- 13 minutes, 44 seconds.

As is apparent, No. 161 again burned for a longer time, the difference being 31% longer.

#### Example 3

To illustrate the effect of the crystallite aggregates in a fuel mixture suitable for igniting charcoal, two mixtures were made up having the following compositions:

|                    | No. 162 |         | Control No. 171 |         |
|--------------------|---------|---------|-----------------|---------|
|                    | Grams   | Percent | Grams           | Percent |
| Aggregates.....    | 300     | 20.6    | 0               | 0       |
| Kerosene.....      | 750     | 51.5    | 750             | 64.7    |
| Water.....         | 400     | 27.4    | 400             | 34.6    |
| Wetting agent..... | 8       | .6      | 8               | .7      |

The wetting agent of Example 1 was used. As is apparent, both mixtures were the same except that No. 171 contained no aggregates and therefore served as the control. No. 162 was made in the way set forth in Example 1, and the control was made by simple mixing. No. 162 was in the form of a spread or flowable paste and in fact was placed in an aerosol can immediately after being made up. The control was in liquid form. About 19.5 g. of No. 162 and 15.5 g. of the control were taken for a burning test in foil cups, these amounts being equivalent in respect of their kerosene content, which was 10 g. in each case. The control burned with a large flame through-

out the test and exhibited a great deal of sparking and sputtering which was considered to be unsafe. Boiling water was visible during the test. It was evident that the control would not adhere to charcoal or other surfaces to which it might be applied owing to its liquid form. No. 162 began burning with a smaller flame which grew larger in a short time but the flame was not as wild as that of the control. There was no sparking or sputtering. The control burned for 6 minutes, 10 seconds while No. 162 burned for 11 minutes, or about 78% longer than the control.

#### Example 4

In another test the nitrate derivative of the aggregates (containing 12.1% nitrogen) was used as the carrier. This material was prepared by mixing 100 g. of the aggregates with 2000 g. of nitrating mix comprising 60.5% sulfuric acid, 25.8% nitric acid and 13.7% water. The resulting mixture was stirred for 1 hour while maintaining the temperature below 10° C., and it was then diluted with 5 volumes of water, filtered, washed with water, and stabilized by boiling in water several times.

A cooking fuel mixture was made up by mixing 4 parts by weight of the derivative with 46 parts of commercial methanol for 4 minutes in a Waring Blendor. Then 12 parts of anhydrous ethanol were added and mixing continued for 1 minute. The mixing was then transferred to a stoppered flask and 10 parts of distilled water added, with shaking. The product was a white translucent gel in which no bleeding or syneresis was noticeable. A similar mixture was made up in the same way except that lacquer grade commercial pyroxylin was used in place of the aggregates nitrate. The pyroxylin had a nitrogen content of 11.2%. The resulting pyroxylin product was in the form of a white milky-looking gel which was bathed in a milky liquid. Twenty grams of each of these cooking fuels were weighed into aluminum foil cups and ignited, and at the same time 20 g. of the commercial material used in Example 1 were also placed in a cup and ignited. The aggregates nitrate mixture burned evenly with a blue flame about 3 to 4 inches high, which towards the end of the burning period became yellowish but not smoky. The mixture burned for 13 minutes, 7 seconds and left a residue weighing 0.06 g. The pyroxylin mixture also burned evenly with a blue flame about 3 to 4 inches high which burned yellowish towards the end of the test. The burning time was 11 minutes, 53 seconds, and the residue was 0.20 g. The commercial mixture burned with a blue flame and exhibited considerable sparking towards the end of the period. The burning time was 12 minutes, 6 seconds and the ash was 0.036 g. It may be seen that the aggregates nitrate mixture had a 10.3% longer burning time than the pyroxylin mixture and an 8.4% longer time than the commercial mixture.

If desired, small amounts of flame-coloring salts or compounds may be added to the fuel mixtures to impart a color to the flame, or to give it a uniform color, and thus increase the attractiveness of the mixtures. Conventional flame-coloring salts are suitable, including those of cuprous copper, thallium, tellurium, strontium, sodium, etc.

Although the invention has been described in connection with specific embodiments of the same, it will be understood that it is capable of obvious variations without departing from its scope.

In the light of the foregoing description, the following is claimed:

1. A fuel mixture comprising a cellulosic carrier, a combustible liquid and water, the cellulosic carrier being selected from the group consisting of cellulose crystallite aggregates and topochemical oxidation, ether, and ester derivatives thereof having a degree of substitution of less than 0.5 and being insoluble in water and the combustible liquid, said cellulosic carrier being non-fibrous, infusible and combustible and having a multiplicity of pores, voids and cracks in the surface thereof by means of which the liquid present is sorbed, the fuel mixture comprising 3 to 45% by weight of the cellulosic carrier, 90 to 40% by weight of the combustible liquid, and 4 to 30% by weight of water, the fuel mixture being in the form of a smooth spreadable mass that is free of bleeding, being adherent to surfaces, having no flash, and having a longer burning time than a conventional cellulose nitrate containing fuel in which the same liquid is present.

2. A fuel mixture comprising a cellulosic carrier, a combustible liquid and water, the cellulosic carrier being selected from the group consisting of cellulose crystallite aggregates and topochemical oxidation, ether, and ester, and ester derivatives thereof having a degree of substitution of less than 0.5 and being insoluble in water and the combustible liquid, said cellulosic carrier being non-fibrous, infusible and combustible and having a multiplicity of pores, voids and cracks in the surface thereof by means of which the liquid present is sorbed, the fuel mixture comprising 10 to 45% by weight of the cellulosic carrier, 80 to 40% by weight of the combustible liquid, 10 to 30% by weight of water and up to 2% by weight of a wetting agent, the fuel mixture being in the form of a smooth spreadable mass that is free of bleeding, being adherent to surfaces, having no flash, and having a longer burning time than a conventional cellulose nitrate containing fuel in which the same liquid is present.

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