Patented Dec. 14, 1937 2,102,005

UNITED STATES PATENT OFFICE

2,102,005

GEL FORMATION

Grinnell Jones, Cambridge, Mass., and Irving B. Rymph, La Grangeville, N. Y., assignors to S. Sternau & Co., Inc., New York, N. Y., a corporation of New York

No Drawing. Application July 25, 1931, Serial No. 553,232. Renewed October 26, 1937

15 Claims. (Cl. 44—7)

This invention relates generally to a process of gel formation and to the product formed thereby, and more particularly to the formation of gels which are adapted for use as a fuel.

The manufacture of alcohol in solid form for fuel purposes has been practised for a considerable period, and many methods of effecting solidification have been attempted. Most of these methods yield a product that is not satisfactory for commercial utilization as a fuel. The method with which best results previously have been attained, and which has proven to be most successful commercially, involved the use of cellulose nitrate as a solidifying agent. The cellulose nitrate was dissolved in alcohol to form a sol which subsequently was gelled by an injection of liquid water. The product so obtained possessed disadvantages which have been overcome by the present invention.

In the previous commercial manufacture of this type of gel, the sol comprising cellulose nitrate and denatured ethyl alcohol was usually run into small containers in which the product was vended. Water under pressure was then injected into the sol in a plurality of fine streams having a velocity sufficiently great to enable most of the water to penetrate to the bottom of the container. The water coming into contact with the sol caused some of the cellulose nitrate to precipitate as a skin, each stream of water causing formation of an irregular skin or sack of cellulose nitrate having water on the inside and liquid colloid on the outside. If immediately after injecting the water the container were turned upside down, most of the original liquid colloid could be poured out, leaving a plurality of these sacks attached to the bottom of the container.

After thus injecting water and forming water containing sacks, covers were placed on the containers and the latter were permitted to stand undisturbed for several days. During this period water diffused through the skins and caused the liquid colloid to set to a gel, and alcohol passed into the sacks. This alcohol never solidified. The formation of a gel under this process was therefore incomplete. There was usually some free liquid on top of the gel and always free liquid in the sacks. Sometimes tubes or channels through the gel were present. The product formed by the water injection process, when placed in a cloth and squeezed, readily yielded its alcoholic liquid, leaving behind a fibrous mass of cellulose nitrate.

The presence of free liquid is objectionable. It creates a risk since it may be spilled while the can is being opened, or during the burning operation, thus increasing the fire hazard and subjecting the user's clothing or furniture to possible damage. Further, such a product requires the use of a container which must be not only competent to hold the solidified gel, but must also be capable of confining liquid.

The disadvantages above outlined have long attended the manufacture of solid alcohol, and they have not been overcome prior to our invention. It is therefore an object of the invention to obviate these disadvantages.

It is an object of the invention to provide a process whereby solidification of a sol is effected with formation of a gel product having enhanced characteristics as uniformity, stiffness, translucence, physical appearance and stability.

More specifically, other objects of the invention are the provision of an improved solidified fuel product which is rich in heat units, easily ignitable, leaves a minimum of residue or ash, burns evenly with little or no smoking or sputtering or odor, which will withstand the usage to which it is subjected in commercial handling without ill effect, will not deteriorate upon standing, will remain solid during combustion, and in which the solid and liquid constituents are inseparable, so that no free liquid is present; and to provide a process whereby a solidified fuel having these and other advantageous features can be manufactured readily and inexpensively.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the product possessing the features, properties, and the relation of constituents, which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

In the practice of the invention, a sol of a disperse substance in a dispersion medium which is preferably an organic substance or mixture thereof is first formed and placed in a suitable container. This sol may be converted to the gel state by subjecting it to the influence of vapors of a non-solvent for the disperse substance. The non-solvent preferably is miscible with the dispersion medium, and when mixed therewith forms mixtures in which the disperse substance does not form a sol. The contact with vapors of a non-solvent may be by means of an atmosphere containing such vapors. This atmosphere may be, but is not necessarily, air, since any suitable

gaseous medium may be employed to sustain the vapors. For convenience of description, the term "atmosphere" is frequently used in the present specification and claims, but it is to be understood that such expression is intended generically to describe air or any other suitable medium, wherever the context permits. After a suitable time, ranging from a few hours to a few days, enough of the non-solvent will have passed from the vapor state into the sol to produce a gel having improved qualities. After gelation is carried sufficiently far to meet the requisites placed upon the product, the gel is removed from the vapor atmosphere.

A suitable disperse substance is a carbohydrate derivative such as a nitro-derivative, for example, a cellulose nitrate of a desired degree of nitration. A cellulose nitrate within the approximate range of 10.0 per cent to 12.5 per cent nitrogen content is satisfactory. While cellulose nitrate of any viscosity may be used, the more soluble grades with a low viscosity are preferred. The amount used may vary from about 0.5 per cent to about 10 per cent, a very satisfactory concentration when using a cellulose nitrate containing 11.6 per cent nitrogen and having a viscosity of 35 seconds being 2 per cent in the sol. Other disperse substances such as cellulose acetate, and the like, may be employed.

The dispersion medium may be any suitable solvent or solvent mixture for the disperse substance used. Thus when preparing a solid alcohol for fuel the monohydric alcohols of not more than two carbon atoms in the molecule are satisfactory solvents when the disperse substance is a cellulose nitrate, for instance, methyl alcohol, ethyl alcohol, or mixtures of the two. In the case of fuel gel formation, a combustible solvent is employed. By this it is meant that the solvent is formed either entirely, or in preponderant amount, of combustible material or materials, such as the alcohols mentioned, so that it is capable of being burned, even though a non-combustible ingredient may be present in sufficiently limited quantity not to destroy the combustible nature of the solvent as a whole.

As a non-solvent, there may be used a liquid possessing a suitable vapor pressure, in which the disperse substance is not soluble and which in mixtures with the dispersion medium in proper proportions prevents the dispersion medium from forming a sol with the disperse substance. Water, for example, is a suitable non-solvent when using a cellulose nitrate dispersed in an alcoholic medium. It will be realized, of course, that choice of any particular non-solvent will be governed by the natures and amounts of the materials present. Thus a hydrocarbon oil such as kerosene, benzine and gasoline, may be used with a properly chosen dispersion medium, as for instance, amyl acetate.

Other disperse substances, dispersion media, and non-solvents suitably fulfilling the herein described general requirements will occur readily to those skilled in the art, and accordingly it is not intended to limit the present invention to any single expressly mentioned ingredient.

While it is within the concept of the present invention to rely upon the final vapor treatment of the sol for the entire gelling effect, it is preferable in many cases to reduce the time required for the formation of the gel by adding a certain amount of non-solvent to the sol before final exposure thereof to the vaporized non-solvent. In forming a satisfactory product it is of importance that the relationship between the disperse substance, the solvents and the non-solvents be such that there is no gel formation before the sol is placed in the jelling atmosphere. Otherwise the finished gel will be lacking in mechanical strength.

Thus, while in accordance with the principles of the present invention one type of satisfactory fuel product may be formed by vapor treating a relatively simple colloid, comprising anhydrous ethyl alcohol and a suitable cellulose nitrate dissolved therein, the invention further contemplates the production of a fuel wherein cellulose nitrate having a proper nitrogen content to render it soluble may be dissolved in a mixture comprising absolute ethyl alcohol, and, if desired, additional solvents, and wherein suitable denaturants and an additional bulk of fuel alcohol containing a small amount of non-solvent may be introduced, the proportions and properties of the ingredients being such that the solvent power of the solvent or solvents in the colloid so formed is sufficient to maintain the same in a liquid state, such colloid being adapted to be solidified to a gel consistency upon final treatment in a humid atmosphere.

As an illustrative embodiment of a manner in which the invention may be practised, the following example is presented:

A sol is prepared containing about 6 per cent of cellulose nitrate having an 11.6 per cent nitrogen content and possessing a viscosity of 35 seconds in anhydrous ethyl alcohol containing sufficient methyl alcohol to promote easy solution, which may be about 16 per cent and, if desired, other denaturants. Sol formation may be facilitated by mixing the cellulose nitrate with a portion of the ethyl alcohol, and then adding the remainder of the ethyl alcohol mixed with methyl alcohol and the other constituents of the mixture.

The cellulose nitrate sol is then diluted with commercial denatured ethyl alcohol to which a desired amount of water has been added, a sufficient quantity of mixed alcohol and water being employed to bring the water content of this admixture to 3 per cent and to reduce the cellulose nitrate concentration to 1.8 per cent. Commercial 95 per cent ethyl alcohol having an added per cent or two of water may be used but this particular water content can be varied to a reasonable extent. It is desirable to add as much water as possible to the colloid at this point, to reduce the time required in the subsequent gelling step, but care must be taken not to add an amount which will cause premature weak gel formations. The maximum water content of the product of this step is dependent upon the solvent power of the dispersion medium. If desired, a suitable dye and/or perfume may be added.

This sol is now poured into suitable containers which are placed in a chamber in which the atmosphere is kept saturated or nearly saturated with water vapor. This chamber is preferably in the form of a long passage through which the containers are continuously moved on wheeled trucks, and through which the humid atmosphere is circulated and recirculated counter-currently to the movement of the containers. There may be some tendency for the ethyl alcohol and methyl alcohol in the colloid to evaporate, but this tendency may be reduced or compensated for by admixing suitable amounts of vapors of ethyl alcohol and methyl alcohol with the water vapors. The proportions of vapors of water, ethyl alcohol and methyl alcohol may be varied within wide limits, one suitable proportion being 10 parts of

water, 2 parts of ethyl alcohol and 1 part of methyl alcohol. The control of the relative amounts of these vapors and the maintenance of desired humidity in the passage may be effected by any suitable known means of air conditioning.

The colloid thus subjected to these vapors gradually absorbs water from a vapor state, and a gel is formed progressively from the upper surface downwardly. The time needed to solidify the entire container varies in accordance with the particular materials used and conditions imposed, ranging from a few hours to a few days. Three days at the most is usually sufficient when the atmosphere is kept near the saturation point.

The containers are removed from the passage as soon as sufficient water has been absorbed to produce a product having the qualities demanded of it. Gelation is not necessarily carried forward to the ultimate degree, but may, when desired, be stopped whenever the product has attained a condition which satisfies the conditions prescribed for it.

The containers used in the final step may be those in which the fuel is vended, in which case it is only necessary to cap and label them after removal from the vapor chamber. An alternative procedure would be to remove the product from the container in which it is gelled, and divide it into portions having any desired shape, after which it can be suitably packaged for distribution. The increased stiffness, uniformity, and absence of free liquid characterizing this improved product admirably suit it for handling in this latter manner.

This described process of solidifying a sol by subjecting it to an atmosphere of a vaporized non-solvent yields a clear, translucent, uniform gelled product having no free liquid on top of or under the gel, and having no sacks or channels of free liquid or weak gel formed therein. The product is stiffer than that made by adding liquid water, and if placed in a comparatively fine mesh cloth and squeezed the gel may be extruded without causing a separation into an alcoholic liquid and a residue of cellulose nitrate. Such improved gel is not disintegrated or damaged by the shocks and vibrations incident to packaging and shipping. The burning properties of the gel can be controlled by a proper choice of constituents. The faults which characterize gels heretofore made by liquid injection, and which workers in the art have long sought to overcome, are obviated in this new product in a remarkable and unexpected manner.

It is to be understood that the terms "solvent" and "sol" when used throughout the specification and claims are used in the general sense, for, strictly speaking, nitrocellulose does not dissolve to form a solution but disperses in a dispersion medium to form a colloidal dispersion.

Also, the term "non-solvent" is used in its commonly understood sense to mean a dispersion medium in which such small amounts of material can be dispersed that such medium is considered for all practical purposes a non-solvent.

It will be seen that there has been provided a process and a product which are admirably suited to fulfill their intended functions, and which constitute a marked advance over the best previous practice relating to the type of gel formation under consideration.

Since certain changes in carrying out the above process, and certain modifications in the composition which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween. Particularly it is to be understood that in said claims, ingredients or compounds recited in the singular are intended to include compatible mixtures of such ingredients wherever the sense permits.

Having described our invention, what we claim as new and desire to secure by Letters Patent, is:

1. A process of forming solidified fuel which comprises dissolving a nitrocellulose in an alcoholic solvent, and solidifying the sol so formed by subjecting it to an atmosphere containing a non-solvent in a vapor state, while retaining substantially all of said alcoholic solvent in the solidified fuel.

2. A process of forming solidified fuel which comprises dissolving a nitrocellulose having a nitrogen content which renders it soluble in anhydrous ethyl alcohol in such alcohol, and solidifying the sol so formed by subjecting it to an atmosphere containing a non-solvent in a vapor state, while retaining substantially all of said anhydrous ethyl alcohol in the solidified fuel.

3. A process of forming solidified fuel which comprises dissolving a nitrocellulose having a nitrogen content approximately ranging from 10 per cent to 12.5 per cent in an alcoholic solvent including methyl alcohol, and solidifying the sol so formed by subjecting it to an atmosphere containing a non-solvent in a vapor state, while retaining substantially all of said alcoholic solvent in the solidified fuel.

4. A process of forming solidified fuel which comprises dissolving a nitrocellulose in an alcoholic solvent, reducing the solvent power by adding a mixture of alcohol and non-solvent thereto, and thereafter solidifying the sol so formed by subjecting it to an atmosphere containing a non-solvent in a vapor state, while retaining substantially all of said alcoholic solvent in the solidified fuel.

5. A process of forming solidified fuel which comprises dissolving a nitrocellulose having a nitrogen content which renders it soluble in a dispersion medium containing ethyl alcohol and methyl alcohol in such a dispersion medium, reducing the solvent power of the sol so formed to a point short of that at which gelation begins by adding a mixture of ethyl alcohol and water thereto, and thereafter solidifying said sol by subjecting it to an atmosphere containing water vapor, while retaining substantially all of said dispersion medium in the solidified fuel.

6. A process of forming solidified fuel which comprises forming a sol containing about 6 per cent of cellulose nitrate having a nitrogen content of approximately 10 per cent to 12.5 per cent in a dispersion medium containing anhydrous ethyl alcohol and sufficient methyl alcohol to promote easy solution, adding to such sol a bulk of ethyl alcohol containing sufficient water to bring the water content of the admixture to approximately 3 per cent, and thereafter solidifying the sol by subjecting it to an atmosphere containing water vapor, while retaining substantially all of said dispersion medium in the solidified fuel.

7. A process of fuel gel formation which comprises forming a sol by dispersing a cellulose derivative such as nitrocellulose or cellulose acetate in a combustible liquid solvent therefor, and solidifying such sol by subjecting the same to the influence of vapors of a non-solvent for said compound, while retaining substantially all of said combustible solvent in the solidified gel.

8. A process of fuel gel formation which comprises forming a liquid colloid by dissolving a cellulose derivative such as nitrocellulose or cellulose acetate in a combustible liquid solvent therefor, and solidifying such liquid colloid by placing a quantity thereof in an open topped container, and keeping said container in an atmosphere containing vapors of a non-solvent for said compound which is miscible with said solvent until a sufficient quantity of said vapors are occluded by said colloid to reduce the solvent power of said sol in an amount permitting gelation of such colloid to the required extent.

9. A process of fuel gel formation which comprises dissolving a cellulose derivative such as nitrocellulose or cellulose acetate in a combustible liquid solvent therefor to form a sol, reducing the solvent power of such solvent by adding thereto a non-solvent for said compound in a quantity short of that needed to solidify the sol, and thereafter solidifying said sol by subjecting the same to an atmosphere containing vapors of a non-solvent for said compound, while retaining substantially all of said combustible solvent in the solidified gel.

10. A process of fuel gel formation which comprises dissolving a cellulose derivative such as nitrocellulose or cellulose acetate in a combustible liquid solvent therefor to form a sol, reducing the solvent power of such sol to a point short of that at which gelation begins by adding thereto a mixture of a solvent and a non-solvent for said compound, and thereafter solidifying said sol by subjecting the same to an atmosphere containing vapors of a non-solvent for said dispersed substances while retaining substantially all of said combustible solvent in the solidified gel.

11. A process of fuel gel formation which comprises dissolving a cellulose derivative such as nitrocellulose or cellulose acetate in a combustible liquid solvent therefor and thereafter solidifying the sol so formed by subjecting it to an atmosphere containing vapors of a non-solvent for said compound in preponderating amount, and containing lesser amounts of vapors of said combustible solvent, while retaining substantially the full quantity of said combustible solvent in the solidified gel.

12. A process of forming solidified fuel which comprises dissolving, in an alcoholic liquid, cellulose having a nitrogen content which renders it soluble therein, placing a quantity of the sol so formed in an open topped container, placing said container in a chamber, introducing water vapor into said chamber for absorption by said sol, and leaving the sol under the influence of said vapor until it solidifies to a required extent.

13. A process of forming solidified fuel which comprises dissolving, in an alcoholic liquid, cellulose having a nitrogen content which renders it soluble therein, placing a quantity of the sol so formed in an open topped container, placing said container in a chamber, introducing vapors of water and alcohol into said chamber for absorption by said sol, and leaving the sol under the influence of said vapors until it solidifies to a required extent.

14. A process of forming solidified fuel which comprises forming a sol containing about 6 per cent of nitrocellulose having a nitrogen content of approximately 10 per cent to 12.5 per cent in a dispersion medium containing anhydrous ethyl alcohol and sufficient methyl alcohol to promote easy solution, adding to such sol a bulk of ethyl alcohol containing sufficient water to bring the water content of the admixture to approximately 3 per cent and to reduce the nitrocellulose concentration to approximately 2 per cent, and thereafter solidifying the sol by subjecting it to an atmosphere containing water vapor while retaining substantially all of said dispersion medium in the solidified fuel.

15. A process of gel formation which comprises forming a liquid sol by dispersing a cellulose derivative such as nitrocellulose or cellulose acetate in a liquid solvent therefor, and solidifying such sol by subjecting the same to the influence of vapors of a non-solvent for said derivative, while retaining substantially all of said solvent in the solidified gel.

GRINNELL JONES.
IRVING B. RYMPH.