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Eckels

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[54] **REVERSIBLE SENSITIZATION OF LIQUID EXPLOSIVES**

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[51] **Int. Cl.** **F42b 3/00,** F42d 1/00, F42d 5/00

[58] **Field of Search** 102/22–24, 102/27, 28; 149/2, 17, 89, 110

[56] **References Cited**

UNITED STATES PATENTS

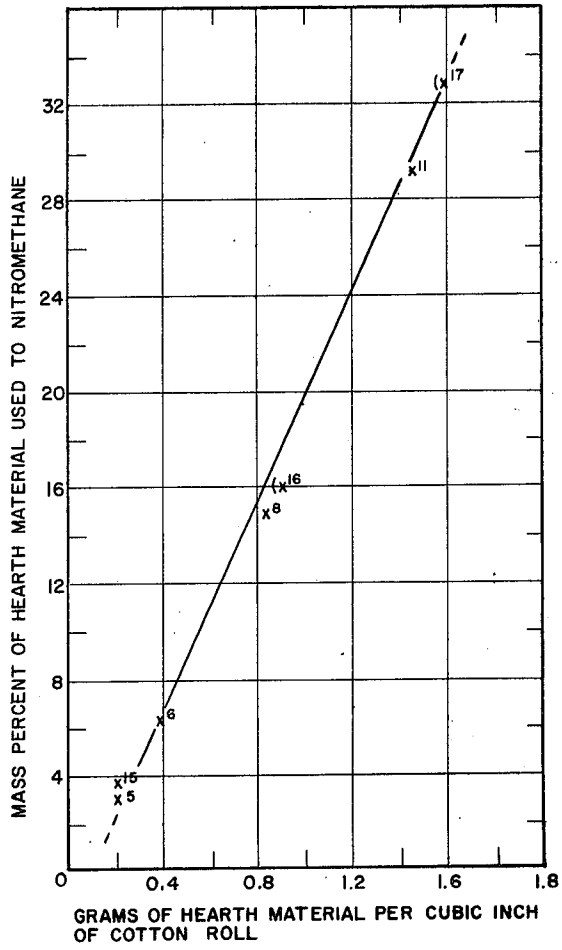
3,456,589	7/1969	Thomison et al.	102/23
3,580,171	5/1971	Maes	102/28
3,667,388	6/1972	Heinemann	102/28

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Attorney, Agent, or Firm—Richard D. Law

[57] **ABSTRACT**

Microspheres spacially suspended in a liquid, not normally considered an explosive, cause a propagating detonation in the liquid, and the liquid is reversed to non-explosive configuration by removal of the microspheres. The microspheres are prepositioned in a predetermined quantity in a porous suspending medium, the quantity being sufficient to cause an overdrive of velocity of chemical reaction to detonate the liquid. The suspending medium with the microspheres may be inserted or withdrawn as desired from the liquid, whereby the liquid with the included medium and microspheres will detonate and the liquid without the medium and microspheres will not detonate.

20 Claims, 2 Drawing Figures



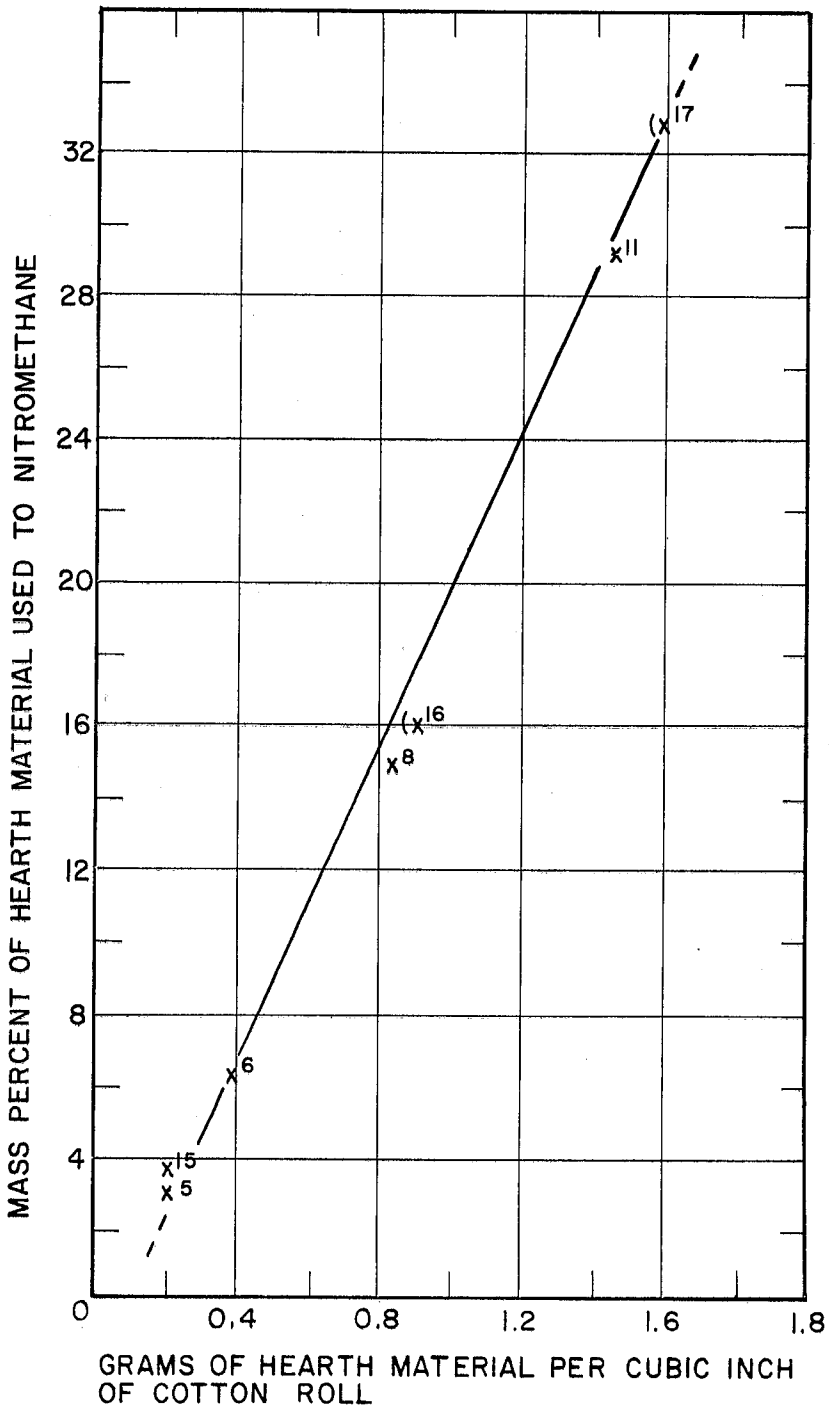

MASS PERCENT OF HEARTH MATERIAL USED TO NITROMETHANE
0
4
8
12
16
20
24
28
32
0.4
0.8
1.2
1.6
1.8
GRAMS OF HEARTH MATERIAL PER CUBIC INCH OF COTTON ROLL
17
11
16
8
6
15
5

Fig_1

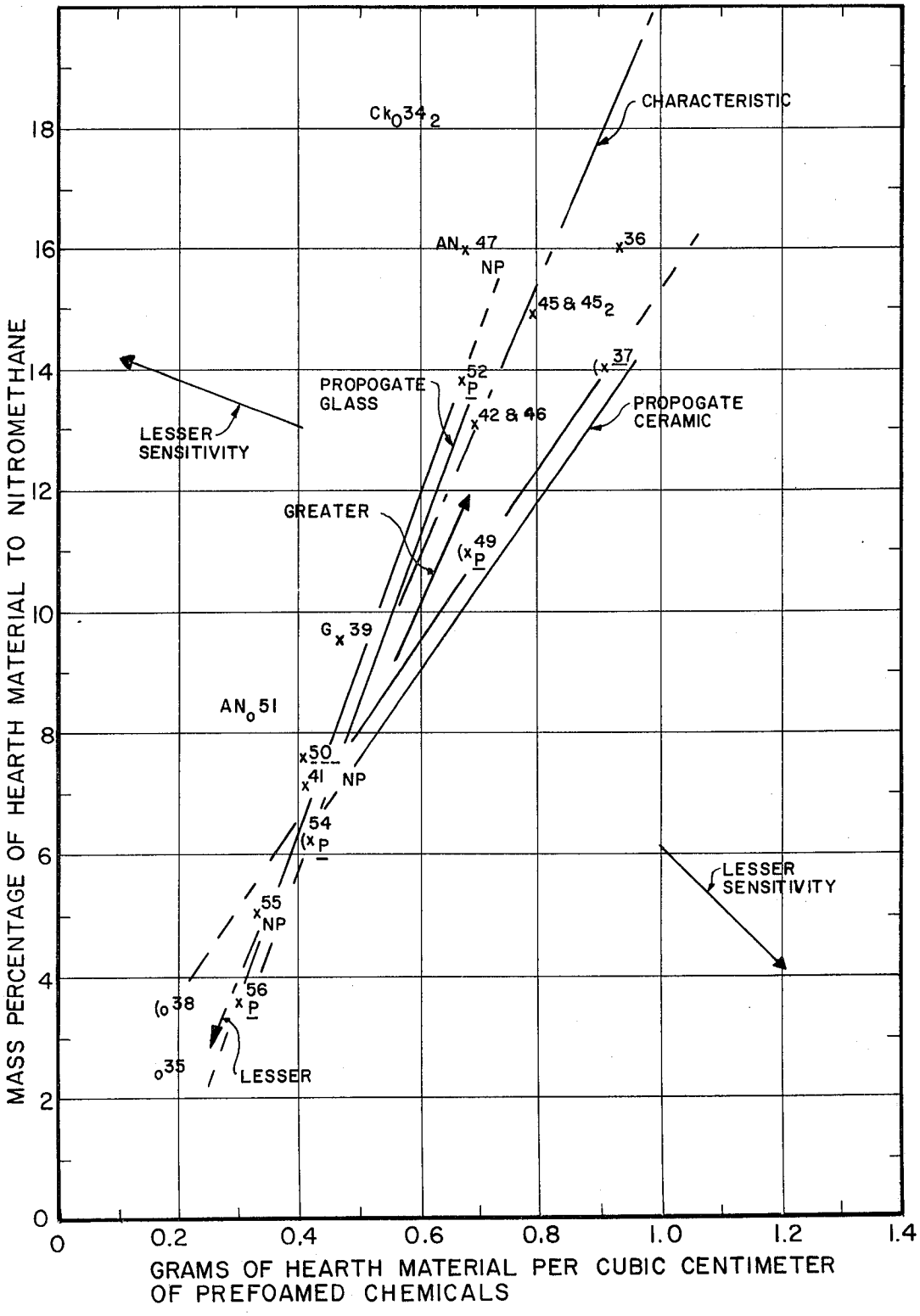

MASS PERCENTAGE OF HEARTH MATERIAL TO NITROMETHANE
GRAMS OF HEARTH MATERIAL PER CUBIC CENTIMETER OF PREFOAMED CHEMICALS
0
2
4
6
8
10
12
14
16
18
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Ck0342
CHARACTERISTIC
ANx47
NP
x36
x45 & 452
PROPOGATE GLASS
x52P
(x37
PROPOGATE CERAMIC
x42 & 46
LESSER SENSITIVITY
GREATER
(x49P
Gx39
AN0 51
x50
x41
NP
54
(xP
LESSER SENSITIVITY
x55
NP
(o38
x56P
o35
LESSER

Fig_2

REVERSIBLE SENSITIZATION OF LIQUID EXPLOSIVES

This application is based on the invention set out in Disclosure Document No. 01137, filed in the United States Patent Office June 2, 1972. This application is, also, based in part on Disclosure Document No. 12792, filed Aug. 17, 1972, in the United States Patent Office.

INVENTION FIELD

This invention relates to a means by which the sensitivity to denotation of liquids, which can be made to detonate, can be increased by the insertion of a physical additive sensitizer to such liquid, and which added sensitizer can be readily and quickly manually removed leaving the liquid essentially as it was prior to the adding of the sensitizer.

DEFINITIONS

Burning or combustion is an oxidation which can take place with ordinary combustibles (such as wood, coal, paper, etc.) but, also, such propellants pyrotechnics, etc. spread out and are not confined. The rate of burning of the propellants and pyrotechnics is between a few millimeters and a few centimeters per second.

A deflagration is an oxidation having a rate of burning (or velocity) of about 1000 meters per second. It has a velocity between "combustion" and a "low-order detonation" which is called an "explosion."

An "explosion" is a chemical reaction or change of state which is effected in an exceedingly short space of time with the generation of a high temperature and generally a large quantity of gas. It produces a shock wave in the surrounding medium, MIL-STD-444. An explosion is a milder form of detonation.

Detonation is defined as "an exothermic chemical reaction that propagates with such rapidity that the rate of advance of the reaction zone into unreacted material exceeds the velocity of sound in the unreacted material, that is, the advancing reaction zone is preceded by a shock wave." When this rate of advance attains such a value that it will continue without diminution through the unreacted material, it is termed a stable detonation velocity. When the detonation rate is equal to or greater than the stable detonation velocity of the explosive, the reaction is termed a high-order detonation. When the detonation rate is lower than the stable detonation velocity of the explosive, the reaction is termed a low-order detonation or "explosion." Solid and liquid explosives which propagate at velocities above 3500–4000 meters per second are usually considered detonating explosives.

The current theory of shock and detonation waves is largely founded on the work of Chapman-Jouguet and R. Becker. The Treatment of sustained detonation, often called the Chapman-Jouquet Theory is based on four assumptions: 1. The detonation approaches the steady state, 2. The flow is laminar and one-dimensional, 3. The detonation products approach a state of chemical equilibrium some distance behind the detonation front; and 4. The detonation velocity is calculated using equations for conservation of mass, momentum and energy.

The critical-charge diameter of a liquid is that at which the attenuating detonation front will not be restored by the wave traveling over the compressed explosive. If the liquid is considered in a tubular container, if the diameter of the container is less than the critical charge diameter, the detonation will cease. If the diameter is larger than the critical one, an outward detonation wave will arise in a certain period of time after transition and the explosive will detonate in the larger volume. For nitromethane this is about 18 mm by experiment and about 14.3 mm. by calculation. The critical diameter for liquid TNT is about 62 mm. The shock loading needed to initiate nitromethane is on the order of 86 to 90 kilobars.

The above definitions are taken from the Encyclopedia of Explosives and Relates Items, Vol. 4, Picatinny Arsenal, Dover, New Jersey, 1969.

Steady State propagation of detonation is ideal or non-ideal. The minimum steady state detonating velocity is, for a particular confinement, attained at the Critical Diameter d below which steady detonation will not propagate. This minimum steady propagating velocity would be nonideal by its definition. As the diameter is increased to larger sized cylinders the steady state velocity increases and it approaches closely the ideal state of steady velocity. These parameters vary from one explosive to another and with the strength and materials of the confining walls of the cylinder holding the explosive.

The sensitizer for reversible use in explosives, according to the present invention, should have a degree of applicability to any fluid explosive, gaseous, liquid, or flowable slurry. However, of chief concern to the invention are liquid explosives. From among liquid explosives the sensitizer may be used to increase sensitivity of non-detonator-cap sensitive or detonator-cap sensitive explosives, in the later case being effective as a booster. However, of prime importance to this invention is the former case of non-detonator-cap sensitive liquids which when joined with the means of this invention can be made to detonate, or explode, from the detonation of a No. 6 cap. These liquids might be further defined a liquid capable of sustaining detonation, after it is initiated at or above a characteristic velocity, being at least its lowest steady state velocity and provided that its diameter normal to the axis of propagation is at least its critical diameter. The non-detonator-cap sensitive liquids of the potentially explosive liquids described can usually be initiated with the impetus from powerful booster charges.

DESCRIPTION OF PRIOR ART

Sprengel types of explosives, consisting of two or more chemicals otherwise non-explosive, which when mixed become detonable, have been known for many years. Various explosive chemical mixtures including nitroalkanes, though more recent, are well known as non-explosives until mixed when they become very effective as detonable explosives from either a blasting cap or booster charge. Several other binary and tertiary chemical mixtures are explosives after mixing and known to the art. However, all of these, which might be classified as Sprengel type explosive mixtures, have the common disadvantage of irreversibility and often involve the handling of noxious chemicals. In addition, some of the mixtures deteriorate with the passing of time. There has been a continuing need for a two or more part explosive system, which is effectively completely reversible, to both include the advantages of the

Sprengel approach, yet be able to return to the "safe" starting condition.

U. S. Pat. No. 2,298,255, granted Oct. 6, 1942, to N. M. Hopkins, discloses numerous liquid mixtures for explosives and a means for mixing them to establish their greater sensitivity. Their sensitization is in fact chemical.

U. S. Pat. No. 3,338,165, granted Aug. 29, 1967, to J. J. Minnick, discloses a non-reversible means of sensitizing nitromethane by the use of phenol-formaldehyde microspheres, "Microballoons," or microspheres of urea-formaldehyde, which are uniformly dispersed in a gel. This disclosure does not show a means where such spheres have been effectively incorporated in other than the gelled composition, which gel, if not included, will allow the balloons to separate by floatation, and become insensitive to detonation. This patent, also, mentions for the resin microspheres certain percentages that are related to the weight of the "composition" which includes the mass of the nitromethane plus the mass of the gelling agent plus the weight of the microspheres. This produces a cumbersome calculation at best, and conceivably non-detonable in some of the compositions shown. Each defined composition is clearly described as a uniform dispersion of such microspheres in a gel. This disclosure does not identify whether or not it may be applicable to potential explosive liquids other than nitromethane. Excepting the broad claim of resin balloons to sensitize nitromethane (which upon simple introduction into the liquid would separate to a non-detonable, by usual means, mixture) all of the other claims of this patent depict a uniform distribution of the resin balloons in a gel.

U. S. Pat. No. 3,687,076, granted Aug. 29, 1972, to J.E. Friant et al., discloses a packaging means for non-explosive liquids and solids which can be field mixed to a detonator sensitivity useful as an explosive.

Numerous other two or more part chemical mixing packages and systems for sensitization are described both in the literature and in patents; however, none of these offer a means of reversing the entire sensitization once it has been accomplished.

In about 1952, F. P. Bowden and A. Yoffe described in some detail theories of localized centers of initiation of detonation as a part of the detonation process. This has been described by numerous others and in the Russian literature.

According to one line of thinking, the hypothesis of local heating, which appears in chemical explosives when under the influence of applied energy, explains the excitation of the chemicals to explosion, or detonation. These local heating areas are called variously "hearths," "energy epicenters," "hot spots," and the like. As the prevalence of these heat centers increases in an explosive, the gross effect is an increase in reaction to eventual explosion, and an increase in the potential heat centers is reflected as an increase in the sensitivity to detonation for such an explosive, up to a point of diminishing returns from attenuating effects of very large quantities. Two of the means by which these heat centers may be developed involve heat from friction involving alien hard particles in the explosive and heating during very rapid compression of bubbles of air, gas, or uncondensed vapor within the liquid.

The heating from friction may be produced by contact of particles in motion from shock causing flow of a liquid explosive. Examples of impurities found useful for this mechanism are sand and carborundum grit and like materials having fusion temperatures well above about 400°C., and having low thermal conductivity. One version of this theory is that the friction in heating appears to be concentrated on jagged points of irregular surfaces of the foreign particles in a manner great enough to cause local decomposition from thermal initiated reaction, in turn causing local shock waves, in turn encouraging added friction and so on until explosion of the entire liquid.

Similarly, adiabatic heating caused by compression of tiny gas bubbles causes thermal decomposition reactions which initiate shock waves, hence compressing further gas bubbles and so on until complete explosion.

Both of these mechanisms seem to have proof from numerous investigators. One of the major points is at least made that shock interactions, usually from external initiating sources, cause localized macro pressures to thereby develop very high temperatures in the liquid's proximity to any variations in homogeneity. The heat centers may propagate, or die out, depending on their size and relative quantity and effect upon the liquid chemicals involved.

In various amounts it has been shown that glass Microballoons, silicon carbide grit, and several different air entraining materials, as well as resin microspheres can increase sensitivity to detonation of most explosives. Microspheres, and other inhomogeneities, are added regularly to many of the slurry explosives now being regularly used to adjust their sensitivity to a desired level, usually high enough for relative ease of initiation.

D. W. Woodhead and H. Titman have show the effect of relatively small channels in the path of detonation of an explosive to increase the velocity of detonation of some explosives. This increase in detonation velocity is caused by the gas in the channel being driven forward in a compressed layer. From time considerations alone a higher velocity would release a higher energy.

SUMMARY OF INVENTION

If the forementioned microspheres are spacially located in a relatively inhomogeneous fashion, and being adequate in numbers, it is believed certain channel effects take place to cause an increase in velocity along with the effects enjoyed by the other mechanisms of friction and adiabatic heating. Another mechanism hypothesized with relation to microspheres of gas, which may be concurrently effective with these other mechanisms, is one of jets where the detonation front is effective against the near side of the sphere in the fashion of a shaped charge to initiate a tiny but high energy jet emitting from the opposite side of the sphere. The channel effect would not normally be expected from a uniform distribution of microspheres nor from very great concentrations of such spheres due to attenuating effects. Very small concentrations of such spheres should not effect channels.

This is to say, it is possible to design a means to include heat centers, which can be placed in a liquid, such as nitromethane, and which can cause the "overdriving" of the velocity of detonation of nitromethane upon initiation with a No. 6 detonator cap placed in the sensitizer means, in a manner that the overdriven nitromethane will propagate in the otherwise unsensitized nitromethane. And more important, for a considerable

distance beyond the sensitizer means causing the overdriving mechanism, the nitromethane will be in a state of high compression and very high velocity and energy dispensation, being equivalent to a new and extremely powerful explosive for that time frame prior to its eventual subsidence to its normal detonating velocity.

In a similar manner, it is possible to sensitize any potential detonable liquid, or liquid mixture, and it is possible to similarly initiate a liquid phase which phases into a liquid flushed oxidizer salt, such as, nitromethane and ammonium nitrate, with the sensitizer means in its "overdriving" configuration, followed by nitromethane, unsensitized, followed by nitromethane flushed ammonium nitrate. In this illustration the entirety should detonate.

The overdriven detonation or sustained detonation described might be properly described as "autocatalytic," at least through that portion of the detonation where the sensitizer is actually involved. Being autocatalytic, it is an explosive reaction, which is accelerated by the action of the sensitizer provided with a rate of reaction increasing until it reaches a stable velocity which incorporates the effects of the inhomogeneities provided. Credited to Mr. R. Carl, it is theorized, the rate of detonation increases more rapidly with increase of density in an insensitive rather than in a sensitive explosive. With a certain dampening effect to any detonation by any liquid, it then becomes desirable to increase the density of a liquid explosive both to increase its detonating velocity and assure its sensitivity to detonation. According to the theory considered, it is believed that the capability is available to increase the density of liquid explosives. It may be theorized that sensitization of the mixtures of this invention might be applicable to explosive materials of gases, desensitized explosive liquids, difficult to detonate explosive liquids, and in variations to initiation adequate for the sensitized volume only to the initiation of overdriving sufficient to initiate the propagation of detonation in an unsensitized fluid.

Among liquids potentially useful with this invention for explosives are many which are cap sensitive but which can be moderated with desensitizers to not detonate from a No. 6 cap but sensitized to a number 6 cap using the methods of this invention. Some of those listed above are not cap sensitive without any desensitizing. Examples of potentially explosive liquids are: Singular chemical systems — Nitroglycerine, Ethylene Glycol Dinitrate, Ethyl Nitrate, Methyl Nitrate, all of which are considered cap sensitive. Nitromethane, dinitromethane, tetranitromethane, dinitropropane, —the first three of which when pure are not considered cap sensitive.

Binary chemical explosive systems — (Sprengel explosives) 87.5/12.5 Tetranitromethane/Benzene, Nitromethane plus 5% Ethylene Diamine, 72/28 Nitric Acid/Benzene, 70/30 Nitric Acid/Methylol, Liquid Oxygen plus a stoichiometric fuel, Mixtures of Nitroparaffins with a Chemical Sensitizer, all of which are considered cap sensitive. Nitromethane plus a chemical desensitizer such as 2% Benzene, any of singular chemical explosive liquids which are cap sensitive plus chemical desensitizing. — such as 70/30 Methyl Nitrate/Methyl Alcohol, — such mixtures that are insensitive by design to the impulse of a No. 6 detonator cap may be mixed to greater or lesser sensitivity to be suited to a use or storage need.

Tertiary chemical explosive systems — Dithekite (any of several mixtures being ratios of Nitric Acid/NitroBenzene/Water i.e., Dithekite 13 is 63/24/13), these can be formed for cap sensitivity and reduced from sensitivity by including a diluent greater amount of nitrobenzene or nitric acid staying inside the miscible phases of the three phase diagram.

Hydrogen Peroxide/Water/(Organic substances such as ethanol) is a family of explosives providing rates from about 750 to 7,000 m/sec when initiated with a booster and a detonating cap. These explosives were investigated by Shanley and Greenspan and the mixtures can be constructed onto triangular phase diagrams which identify detonation regions.

It is an object of this invention to provide a means for mechanically sensitizing a liquid explosive, such as nitromethane, to detonate when subject to the energy release of a No. 6 detonator cap, or other source.

Another object of this invention is to provide a means for mechanically sensitizing a liquid explosive and to be able to remove a mechanical sensitizing means from a potentially explosive liquid, restoring it to insensitivity from detonator cap sensitivity, by simply withdrawing such means from it.

Another object of this invention is to provide a means for mechanically sensitizing potentially explosive liquids and then desensitize such potentially explosive liquids any number of times until ready to detonate them or return such liquids for storage or transport as non-explosive liquids.

A further object of this invention is to provide a means to ship innocuous chemicals and mechanical components to any place, not requiring explosive storage or shipment and eventually requiring only a detonator cap or detonator cord to initiate detonation, all, to the placation of foreign and domestic governmental bodies.

It is still another object of this invention to provide a means wherein explosive devices, such as shaped charges, may be preloaded with non-explosives and reversibly armed for detonation or storage at will.

It is another object of this invention to reversibly sensitize a portion of a potentially explosive liquid, such as nitromethane, in a manner that the resulting detonation rate and energy release, when detonated, is sufficient to propagate detonation in the otherwise untreated liquid where above its critical detonating diameter minimums.

An additional object of this invention is to disperse either gas containing or non-gaseous micro-inhomogeneities in a mini-irregular, but overall regular manner in a potentially explosive fluid to sensitize it to detonation from a 6 blasting cap or similar detonating charge.

It is a still further object of this invention to provide a means for a one time reversible sensitizing of a potentially explosive liquid providing a time dependent means of autosterilization.

A further object of this invention is to accomplish the above and other objectives in an improved and economic manner to reduce explosive use costs while increasing safety and convenience; additional objects may be evident in the course of the further discussion.

These and other objects and advantages of the invention may be readily ascertained by reference to the fol-

lowing description and appended illustrations, in which:

FIG. 1 is a graph of a plot of quantity of hearth material per cubic inch of cotton roll against the mass percent of hearth material to liquid nitromethane; and

FIG. 2 is a graph of a plot of quantity of hearth materials per cc of prefoamed chemicals against the mass percentage of hearth materials to nitromethane.

In general, the present invention pertains to the discovery of a reversible means of increasing sensitivity to detonation of potential liquid explosives, such as nitromethane, by intimately dispersing hearth materials such as Microballoons, glass microspheres, ceramic microspheres, and/or silicon carbide grit in the liquid as in a roll of thin strip cotton, or other equivalent highly porous and permeable material. Such material requires mechanical integrity when placed in a small porous sack, otherwise permeably bound, or in an open cell plastic body, preferably a non-rigid, foam insoluble in the liquid explosive involved. The cotton roll holds the inhomogeneities in place by friction. The intimate dispersion is accomplished in a manner that spacial placing of the inhomogeneities includes a consistency of irregularities in a mini-view (small localities), such as observable under a high powered magnifying glass.

In a plastic foam, such as polyurethane open cell foam, the inhomogeneities are actually incorporated into the thin foam webbing and strands. More webbing is evident with fewer strands than without the inclusions.

Importantly, adequate amounts, with respect to percentage of explosive liquid, of the microspheres are needed in order to accomplish overdriving the detonation velocity to provide propagation throughout the liquid where desired. It has been noted that minor amounts, lower percentages, of microspheres added to urethane foams have given detonation (or no detonation) of a non-definitive character, even using larger impetus than a No. 6 cap. A similar effect has been noted with urethane foams with no inhomogeneities added. In a like manner, the cotton rolls without inhomogeneities did not define a means of sensitization.

Various levels of sensitizing are possible depending on percentages of hearth sources used and their dispersion. In some sensitizer mixes, the detonation around the heat centers (hearths) actually slows and stops. In some, it reaches useful levels but continues only in the region of suspended particles, and is therefore of limited use. But in others, the mix gives rates and energy release high enough to continue detonation in the otherwise untreated liquid depending on the minimum detonating character of the particular material.

The following examples show the operation of the invention, primarily using nitromethane (NM) as the liquid potential explosive and microspheres (mb).

EXAMPLE I

A small container, formed of plastic, metal or the like, is partially filled with about 46 cc of nitromethane. A strip of cotton is sprinkled with about 3 weight percent of glass microspheres, and then rolled into a small cylinder. This cylinder is lightly tied into the roll and then inserted into the liquid nitromethane. The container is placed on a ½ inch steel disc, about 8 inches in diameter on test firing range. An electrically fired No. 6 cap is inserted in the cotton roll, and the lead wires attached. The cap is detonated electrically, and the results of the subsequent detonation examined. The result is shown in the graph of FIG. 1 and point number 5 in the following Table I. Other examples are shown in the Table, including the quantity of liquid nitromethane, the type of carrier for the hearth, the type of hearth and result.

The size of the booster for a particular explosive should be at least the diameter of the liquid explosive's Critical Diameter at the temperature and confinement selected. And the Length should be its Critical Length

TABLE 1

Graph point No.	Volume of NM in cc.	Carrier	Hearth material, percent of NM	Target volume S= Sensitizer area only	Result
1	46	Polyurethane foam	None	S	Low order explosion.
3	46	Rough cotton	do	S	Negative.
4	46	Smooth cotton	do	S	Do.
5	46	do	Plus 3% glass mb	S	Detonation bent ½" Iron.*
6	46	do	Plus 6% glass mb	S	Detonation*.
8	46	do	Plus 15% glass mb	S	Do.*
11	46	do	Plus 29% glass mb	S	Do.*
15	46	do	Plus 3% ceramic mb	S	Low order explosion.
16	46	do	Plus 16% ceramic mb	S	Detonation.*
33	46	do	Plus 33% Ceramic mb	S	Do.*
34½	46	Polyurethane foam	Plus 18% cork tlnes	S	Negative.
35	56	do	Plus 2.4% glass mb	S	Do.
36	50	do	Plus 16% glass mb	S	Detonation.*
36½	46	do	Plus 15% glass mb	S	Detonation, low order—poor form.
37	50	do	Plus 14% ceramic mb	S	Detonation.
38	46	do	Plus 3.5% ceramic mb	S	Negative.
39	46	do	Plus 9.5% SiC grit	S	Low order explosion.
40	12	do	Plus 30% exf. vermlculite		Negative.
41	46	do	Plus 7% glass mb	S	Detonation.
42	46	do	Plus 13% glass mb	S	Do.
39½	20	do	Plus 30% SiC grit	S	Negative.
45	46	do	Plus 15% glass mb	S	Detonation.
46	50	do	Plus 13% glass mb	S	Do.
47	50	do	Plus 16% glass mb S+6" ext.**	S	Detonation only, no extension.
49	56	do	Plus 11% ceramic mb. S+6" ext.**		Detonation, blew hole thru plate.
50	20	do	Plus 7C% glass mb	S+6" ext.**	S detonation only, no extension.
51	46	do	Plus 8C% glass mb. plus 25% AN	S+6" ext.**	Negative.
52	46	do	Plus 14% glass mb	S+6" ext.**	Detonation, blew hole thru plate.
53	40	NM only after sensitizer removed			Negative.
54	46	Polyurethane foam	Plus 6.2% ceramic mb	S+6" ext.**	Detonation, blew hole thru plate.
55	46	do	Plus 4.9% glass mb	S+6" ext.**	S detonation only, no extension.
56	46	do	Plus 3.6% glass mb	S+6" ext.**	Detonation blew hole thru plate.
49C G1		do	Plus 11% crushed glass foam	S+6 ext.**	S detonation, no extension.
G Fm10		Glass foam-opened	=15.9% min. hearths	S	Detonation.
G Fm12		do	=15.3% min hearths	S	Do.
49½		Polyurethane foam	Plus 11% ceramic mb. plus 270 gm. AN in ext.	S+6" ext.**	Excellent detonation.

**Extension is 3"± ID resting on ½" steel plate in addition to sensitizer volume.

or greater; however, as a practical matter if the length is not less than about three times the Critical Diameter it will usually be greater than the Critical Length. In the case of NM the Critical Length is less than this somewhat. Since Critical Length is largely experimentally determined for a particular explosive and conditions and this may be altered by the type of impetus, it probably should be avoided in the application — the more important parameter being the Critical Diameter.

The foam used for the graph of FIG. 2 is a polyurethane sold by Upjohn Company, Kalamazoo, Michigan under the tradename of CPR-2036. This is sold as a two component system, used on a 50/50 ratio to form a lightweight, open cell foam.

The glass microspheres used had an average of 0.28 gm/cc particle density and had sizes in the range of about 10 to 300 microns. The ceramic microspheres had a particle density of about 0.6 gm/cc and sizes from about 60 to 35 micron. From the above tests it is evident that sensitizing to detonation is possible for a range of from about 3 ½ to 30 percent for glass microspheres and about 3 to 33 percent for the ceramic microspheres, if sensitizing NM. It is most important that from about 6 to over 11 percent by weight of ceramic microspheres to weight of nitromethane indicates to initiate detonation with such force as to initiate beyond the sensitizer area (liquid in the carrier) into stock nitromethane with continuing propagation. Similar effects are evident in the range of 3.5 to 14 percent of glass microspheres being nearly as effective. Though higher percentages of each should, also, cause this effect, it begins to engage unfavorable economics.

Ammonium Nitrate (AN) added to the sensitizers did not enhance the effectiveness, though detonation was achieved in some instances. On the other hand in initiating into AN from the overdriven velocity liquid NM where the AN is flushed with NM initiates very well, detonating still above the velocity usual to NM for the distance considered, in the extension described.

It can be reasonably inferred that 0.1 to about 10 percent of Silicon Carbide grit incorporated into a suitable inhomogeneous matrix will sensitize NM to detonation with a No. 6 cap.

Using larger caps, such as a No. 8 cap with about 140 percent as much loading as a No. 6 cap, or boosters of even greater dimensions can allow each level of performance to be greater, to that point where NM can be initiated from boosters alone, if large enough. However, the No. 6 cap is widely available and the utility of my invention requires detonation be available to this small size, if using nitromethane.

It is recognized that silica flour, ground balsam, fired ceramic flour, and other such materials providing hearths can be used with or without microspheres.

While there are many liquid explosives and liquid explosive mixtures which can be used with such a reversible means according to the invention, specifically they include: desensitized nitroglycerin and other nitric acid esters, nitroalkanes, including nitromethane and mixtures of nitroalkanes, liquid oxygen (LOX) liquid explosive mixtures, Sprengel type explosive mixtures, EGDN, isopropyl nitrate, Dithekite, hydrazine or hydrazine nitrate containing explosives, etc.

The foams useful for the invention should be insoluble in the liquid for the potential explosive and have open pores. These foams should maintain foaming capability and structural integrity after addition of necessary extraneous inhomogeneities (microspheres, etc.) to either the foam precusor mix or one of the mix components. Several inorganic foams can be substituted in these sensitizers but open cell resilient plastic foams, such as polyurethane foam, seem to offer advantages in handling.

In suspending by friction, such as in rolls or folds, materials with merit include cotton, loose woven materials as felts and gauzes, metal gauzes, rock wool, etc. Glass fiber materials can have some application; however, glass wool rolls would better retain the hearths.

It has been found impractical, if not impossible, to relate the percentage amount of microspheres, for instance, to the amount of materials to be foamed. This parameter is actually quite insignificant for the reason that mixing a predetermined amount of microspheres with a known amount of foamable chemicals, once foamed may have different volumes, depending not only on temperature, humidity, and actual chemical variations, but on means of mixing, order for mixing, vibration during set, and numerous other factors. Accordingly, this would change the percentage of heat centers relative to the gross volume of explosive liquid. It has been found that the only means to adequately control the degree of sensitization attained from these inhomogeneities is to control the percentage by weight of such inhomogeneities as microspheres used to the weight of liquid explosive, such as nitromethane, being sensitized, whether these heat centers are included in a flexible open cell plastic foam or rolled in a roll of cotton to give a mini-non-conformity to their distribution within the sensitizing volume.

It has been found that one unique source of these heat centers, suitable for inclusion in the open cell plastic foam, is ground closed cell foam glass, Foamglas. This unique material provides the characteristics of both microspheres, having minute bubbles in the particles, and grit or other sharp edged material. I have found that this material is effective, suspended in similar amounts, as effective quantities of microspheres where the material is rough ground to only 10 percent passing a 75 micron particle size.

In sensitizing liquid explosives to detonation from a No. 6 cap, for a liquid which is not otherwise this sensitive, it is found that certain rigid closed cell foams, such as the glass insulating foam made by Pittsburgh-Corning, identified as Foamglas, can, with alteration, be made to provide sensitization of liquid explosives. In turn, this means when removed from the explosive, renders it back to its original state of insensitivity. This means, also, meets the parameter of variable uniformity as far as the hearths are concerned. In fact, the variable uniformity on a mini-basis is inherent in the product.

The way in which this means is developed involves taking a portion of the rigid closed cell material, Foamglas, and subjecting it to the preselected hydrostatic pressure necessary to give a desired amount of breakage of the internal walls of the cells. This pressure is applied for a time sufficient for the complete breaking of the foam walls. The material is depressurized, drained and dried. Depending on the amount of the pressure which is applied, a greater or lesser number of internal walls within the rigid closed cell foam will be ruptured making a part of the rigid material open celled and a part of it closed cell. The remaining closed cells, after

the treatment, are usually smaller than the cells which have been hydraulically breached; however, this is basically a function of wall strength with respect to the exposed area to the pressure and the pressure. After the treatment, that material has, for sensitization characteristic advantages, many sharp edges and points (which have been developed by the breached walls), minute particles, within the foam (which serve as inhomogeneities and which are developed by the breaking of internal walls), and residual closed cells, including many ranging down to even submicron sizes. All of these serve collectively to provide energy centers, as the shock wave passes over them on initiation.

It was found that the sensitivity to detonation can be increased as a sensitizer (for a particular explosive) by changing its character, up to a point, by the increased amount of hydrostatic breaking employed, including greater pressure and longer times. At an optimum, the sensitization will be sufficient to cause detonation at a velocity greater than the steady state detonating velocity for the involved liquid explosive. This is the condition of "overdriven" velocities, which allows propagation beyond the sensitized area. For closed cell rigid foams, which have been treated with lower pressures, sensitivity to detonation of nitromethane will decrease with the lowering of such pressures until it reaches a point of incompetent detonation, or none at all. This lower pressure will vary with the matrix material of the foam, but the Foamglas, pressures below about 250 p.s.i. become increasingly ineffective.

Examples of the validity of the concept are samples of Foamglas of two inches long by 2 inches OD. Each was subject to 400 p.s.i.g., drained, dried at 450°F. for two hours and weighed. They are identified as GFm10 and GFm12 on the examples shown above. Their calculated minimum closed cell porosity respectively was 14.2 and 10.3 percent; however, empirical estimates placed these minimums at 15.9 and 15.3 percent. It is rather more important to relate the effective sensitization attained to the pressure and breaking time used. For practical considerations, a maximum pressure to be effective would be about 1,000 p.s.i.g. for five minutes.

Other rigid closed cell foams are worthy of consideration for this technique including sulphur, ceramic, and rigid plastic foams. Advantages of low cost attend the glass foam, sulphur and some of the plastics.

According to the invention, I have found a way to make an explosive which autosterilizes without creating any light, sound, or smoke, during the self-sterilizing. It has been discovered that there is a variation of the reversible means described above. This variation allows one-time reversing of sensitizing when this may be required. One-time reversing is equivalent to auto-sterilization of the explosive, and where the reversing means mentioned in the text above depends on the physical removal of the carrier and heat centers, the one-time reversibility uses a carrier, foam or roll, which is soluble, in a predetermined time in the potentially explosive liquid. Once the carrier is dissolved, the particles will separate by floatation or settling. When the sensitizing nuclei have coalesced they will no longer serve to sensitize the liquid. That is, the detonator may function but will not initiate the main charge. Alternately, during the time period prior to the dissolution of the foam, such as a tar foam in nitromethane, and after the foam is flooded for use with liquid explosive, it can initiate the main charge directly from the detonator. In this means, as in the others, a mini-irregularity is expected in the dispersion of the hearths.

To employ this invention, the sensitizer, such as microspheres in adequate proportion in a polyurethane open cell foam, is submerged and saturated in the liquid explosive. It is caused to maintain this position, as some will tend to float and others tend to sink, by any suitable means. A detonating cap, Primacord, primer, or other shock source must be inserted into the approximate center of the sensitizing assembly to initiate the explosion. If not detonated, the sequence may be reversed, in which instance the detonator is removed, the liquid removed from the sensitizer by draining or, if flexible, squeezing. As one example, if the sensitizing material is used in a tube, such as a detonating cord, it may be desensitized by simply allowing the liquid to drain out, or blowing it out with air. The removed liquid is desensitized to its original state, and it is safe for its recommended storage. The sensitizer at this point should not have sufficient liquid left in it to sustain detonation even if it were accidentally initiated. The matrix will usually be water insoluble, in which case the sensitizer may simply be washed in water and replaced on shelf storage. If it is desired to reactivate the liquid to an explosive by sensitizing, the sensitizer is simply reimmersed in the liquid and it is ready to use. This reversibility can be repeated as often as desired until it is desired to use the activated liquid explosive — activated, meaning sensitized. The detonator cap can initiate the liquid, such as nitromethane, by simply being initiated after submerging the sensitizer in the NM with the cap in the middle of the sensitizer.

This system provides a means for transporting the non-explosive precursors of an explosive system. The mixing is easily done in situ of the explosion. The explosive mixture is easily deactivated or desensitized, if the explosion is not thereafter needed. Subject to the level of sensitization of a particular mixture employing this means and to the character of the potentially explosive liquid involved, relatively smaller diameters with high orders of sensitization can be identified as critical diameters for specific mixtures. Accordingly, for a mixture or liquid which might support detonation if having a one-inch critical diameter for that portion of the liquid employing the means herein may be reduced to one-eighth to one-quarter inch or less where the sensitizing mixture is immersed in the liquid.

DETAILED DESCRIPTION OF DRAWINGS

The following code indicates the meaning of the points on FIGS. 1 and 2:

X with no marking = Glass microspheres
C = Ceramic microspheres
Numeral = Test number
G = Silicon Carbon Grit
AN = Ammonium Nitrate added
P = Detonation and Positive Propagation Evaluation beyond Booster
NP = Detonation and Negative Propagation Evaluation beyond Booster
x = Detonation in Booster
o = No detonation in Booster

It can be noted from the graph, FIG. 2, the percentage of inhomogeneous material, such as microsphere to

the nitromethane, by weight, is plotted against the weight of such inhomogeneous material per unit volume of prefoamed chemicals. The principal characteristic of this curve is much more subordinate to the percentage of hearths to the weight of NM than it is to the starting conditions of the mix; however, the two together define, for each type of materials used, and show a characteristic slope indicating greater sensitivity as their values increase to some uneconomic point. It can be seen from these lines that, in the event a particular value of the prefoamed condition did not develop into the anticipated volume, the point would fall above the lines into the area of lesser sensitivity, if any at all, such as point No. **34**, or **51**. Likewise, if the material foamed much more than was usual or expected, making less dense foam, the point would fall well below the line and, also, into an area of lesser sensitivity, if any at all.

Of unusual importance, it is noted from about point No. **54** to about point No. **37**, on the ceramic microsphere line, and approximately point No. **56** to approximately point No. **52** on the glass microsphere line, propagation beyond the area of initiation and sensitization is indicated. This is that area in which overdriven velocities of detonation can be expected, sufficient in the case of NM to propagate without other sensitization.

Considering FIG. **2**, the graph of material added per cubic inch of cotton roll against percentage of material to NM in weight, it is noted that line is still very much a straight line for the values considered. It is noted that the sensitization to detonation for NM was the only parameter for these tests and identified on the graph.

PREFERRED EMBODIMENTS

In the preferred embodiments of this invention, it must be considered that first it is quite important for a No. 6 detonator cap to be able to initiate the sensitized explosive, as this is the size of cap often used in commerce. While other larger caps are available, they are more expensive and less readily available. A No. 6 cap might be expected to contain in the order of 4.9 grains of PETN in its base charge. All of the test work and data shown above for this invention have employed No. 6 caps.

For the highest performance in sensitizing a liquid explosive to detonation, a preferred construction of the sensitizer would be similar to that shown as point No. **49** on the ceramic microsphere graph line. Similarly, any of the mixes indicated by the double bar lines, for either the glass or ceramic microspheres, would be considered as preferred ratios, in that within those areas not only is the NM initiated with a No. **6** cap, it is very substantially overdriven at a velocity to cause it to behave very much like a crystalline military HE indicating a major increase in energy release. This overdriving effect represents a velocity in excess of ten percent greater than the normal steady state velocity of detonation of NM, and, in fact, causes continued propagation in diameters above the critical diameter without other sensitizing. The overdriven effect continues for some distance beyond the sensitized area offering major potential in the use of this method for shaped charges and other special explosive devices requiring very high velocities and high energy releases.

In the use of the urethane open cell foam, including microspheres, as indicated, mechanical means will have to be provided to hold the sensitizer submerged in the liquid explosive. With the cotton roll means, a means is needed to prevent it from sinking in the liquid. A simple means for both of these is a wedge of wood or other material in the event the sensitizer is not snug fit to the liquid explosive container.

A preferred embodiment, from a view of economics alone, for the sensitizing suggests these rigid foams which are subjected to intercell breaking as mentioned above. Of these Foamglas appears to be an excellent candidate.

It is important to consider the advantages of frangible microspheres as the hearths, preferably of crystalline materials for what appears to be added hearth effects from tests. It appears that there is somewhat greater sensitizing available from glass microspheres over resin microspheres or grit, and somewhat greater sensitizing appears to be evident from ceramic microspheres over those of glass, with other optimums being considered.

A ceramic microsphere filled foam within the limits of applicability for creating overdriving velocities may combine numerous inhomogeneities for its favorable behavior which include the service of pressure centering, adiabatic heating of included gases, sharp debris from microsphere collapse, with friction and point heating, and in sufficient indicated quantities and proximities including mini-irregularity in dispersion to suggest channel effects and micro-jets. Collectively, such preferred construction will reduce initiation requirements without creating any oversensitization or hazard. It is important to observe that mini-channels could hardly exist using low to very low concentrations of microspheres, though sensitization to detonation might still be achieved for the volume of the sensitizer itself in some lower concentrations.

A preferred method of mixing the hearths, microspheres, etc. into the urethane foam would be to first mix the weighed hearths in the predetermined desired amount, considering the percentage to liquid explosive being sought, into the polyol, or active hydrogen, phase in an intimate manner, then quickly blend in the isocyanate and withdraw to allow the foam to expand and cure. During the cure this is particularly fragile and should not be disturbed until its strength has been completely developed. After cure, a cap well is drilled, as about a ¼ inch diameter hole, to about one inch deep into the sensitizer.

Since the mechanics of creating a mini-nonuniformity of the hearths where they are included in the plastic foam rely entirely on the final percentage of the hearths to the liquid explosive by weight, any plastic which can be foamed to provide these pen cells still entraining the heat centers in the method required would be suitable for this; however, urethane is considered one of the preferred foams to use for this purpose.

What is claimed is:

1. A reversible explosive system sensitive to a number 6 cap comprising

a. a container,

b. a body of a normally non-sensitive liquid potential explosive in an amount sufficient to produce a diameter in excess of about such liquid's critical diameter in said container, and

c. a sensitizer-booster including a permeable body of a size to telescope in said container and absorb at

least some of said liquid, and from about 3 weight percent to 33 weight percent of hearth material in relation to the quantity of absorbed liquid dispersed throughout said permeable body, said permeable body being arranged to be inserted into and withdrawn from said liquid for desensitizing the same and be relieved of its absorbed liquid for desensitizing said permeable body.

2. A reversible explosive system according to claim 1 wherein said permeable body is a loose roll of cotton.

3. A reversible explosive system according to claim 1 wherein said permeable body is an open cell, foamed synthetic resin.

4. A reversible explosive system according to claim 3 wherein said foamed synthetic resin is a polyurethane.

5. A reversible explosive system according to claim 1 wherein said hearth material is glass microspheres.

6. A reversible explosive system according to claim 1 wherein said hearth material is ceramic microspheres.

7. A reversible explosive system according to claim 1 wherein said hearth material is silicon grit.

8. A reversible explosive system according to claim 1 wherein said hearth material is ground closed cell foam glass.

9. A reversible explosive system according to claim 1 wherein said liquid is nitromethane in a large excess of the amount absorbed by said porous body and at about 3 weight percent of ceramic microspheres are supported in said porous body whereby to overdrive the detonation in said nitromethane to produce a propagated detonation throughout the nitromethane in excess of that described in said porous body.

10. A reversible explosive system according to claim 1 wherein said body of a normally non-sensitive liquid is substantially greater than the quantity of liquid absorbed by said porous body.

11. A reversible explosive system according to claim 1 wherein said permeable body is a closed cell body having sufficient cells ruptured to provide the necessary hearth material for said detonation.

12. A method of propagating detonation throughout the body of a liquid explosive in which the velocity of detonation is overdriven by at least about 10 percent excess over normal steady state velocity in the liquid, comprising

forming a small body of explosive liquid having a diameter at least as great as its critical length;

forming a liquid explosive absorbing carrier for from 3 to 33 weight percent of spaced hearths to weight of said small body of liquid explosive, which carrier is capable of absorbing said small body of liquid explosive;

placing said carrier with said spaced hearths in a large body of said liquid explosive; and detonating said small body of liquid explosive in said carrier in said large body of said liquid explosive to cause propagation of detonation throughout said large body of liquid explosive.

13. A method according to claim **12** wherein said liquid is nitromethane.

14. A method according to claim **13** wherein said hearths are 4–14 weight percent of glass microspheres.

15. A method according to claim **13** wherein said hearths are 5–11 weight percent of ceramic microspheres.

16. A method of autosterilizing a liquid explosive comprising:

forming a booster for said liquid explosive containing a sufficient quantity of hearths in spaced relation to sensitize said liquid explosive to detonate, and being formed of a material which absorbs said liquid explosive and dissolves therein; and placing said booster in a body of said liquid explosive, whereby if not detonated within the solubility time of dissolution of said material in said liquid explosive, said spaced hearths are released from their sensitizing spaced relation.

17. A method of sensitizing a liquid explosive comprising

forming a body of a closed cell, rigid foam; subjecting said body of foam to fluid pressure at a sufficient pressure and for a sufficient time to rupture sufficient cells to absorb an amount of liquid explosive sufficient to form a critical diameter and critical length body of liquid explosive and provide sufficient edges of ruptured cells acting as hearths to sensitize the absorbed liquid;

placing said foam body in a body of liquid explosive, and then detonating said foam body while in said liquid explosive.

18. A method according to claim **17** wherein said rigid foam is a foamed insulating glass.

19. A method according to claim **17** wherein said liquid explosive is nitromethane.

20. A method according to claim **19** wherein said foam is foamed insulating glass having a 2-inch length and 2-inch diameter, ruptured at about 400 psi.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,797,392 Dated March 19, 1974

Inventor(s) Robert E. Eckels

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

Col. 1, line 13 - "denotation" should be --detonation--

4 34 - "show" should be --shown--
5 46 - "above" should be --below--
6 55 - Before "6" insert --No.--
11 62 - "floatation" should be --flotation--
14 54 - "pen" should be --open--
In Table I - Line 34, "plus 18% cork tlnes" should be --plus 18% cork fines --
" " " line 50 "7C%" should be --7 1/4%--
" " " 51 -"8C%" should be --8 1/4%--

Signed and sealed this 13th day of August 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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