Aug. 14, 1962 H. J. STARK 3,049,454

LOW DENSITY CELLULAR EXPLOSIVE FOAM

Original Filed Aug. 15, 1955 3 Sheets-Sheet 1

FIG. 1.

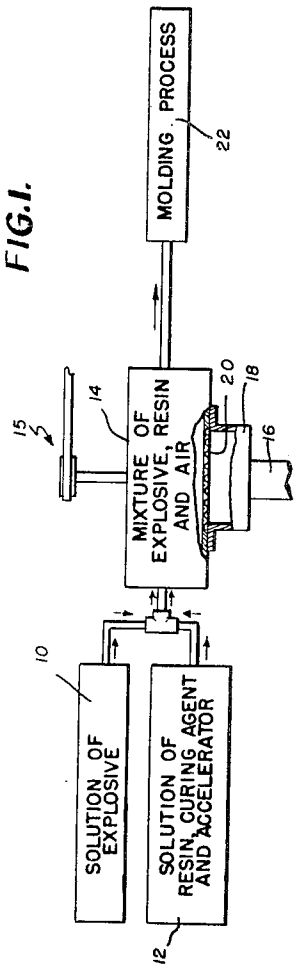
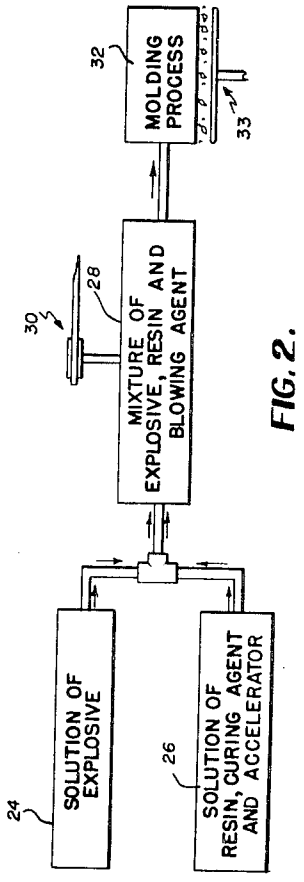


FIG. 2.



INVENTOR.
HOWARD J. STARK
BY
George Sipkin
ATTORNEY

LOW DENSITY CELLULAR EXPLOSIVE FOAM

Original Filed Aug. 15, 1955 3 Sheets-Sheet 2

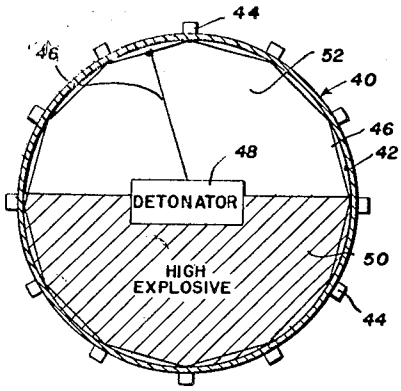


FIG. 3.

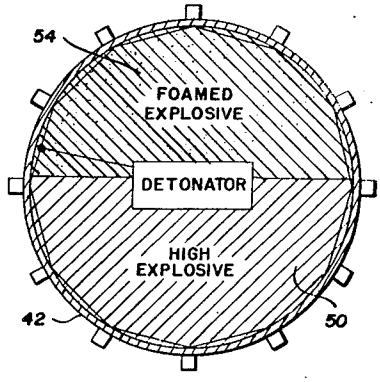


FIG. 4.

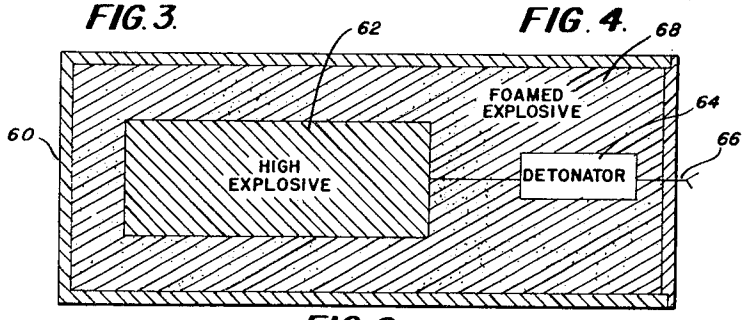


FIG. 6.

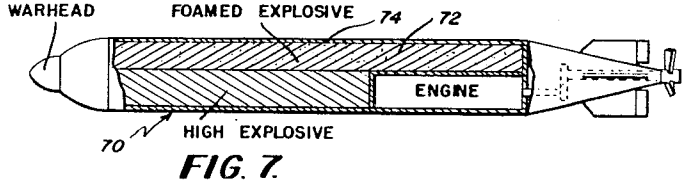


FIG. 7.

INVENTOR.
HOWARD J. STARK
BY George Siptin
ATTORNEY

LOW DENSITY CELLULAR EXPLOSIVE FOAM

Original Filed Aug. 15, 1955 3 Sheets-Sheet 3

FIG. 5.

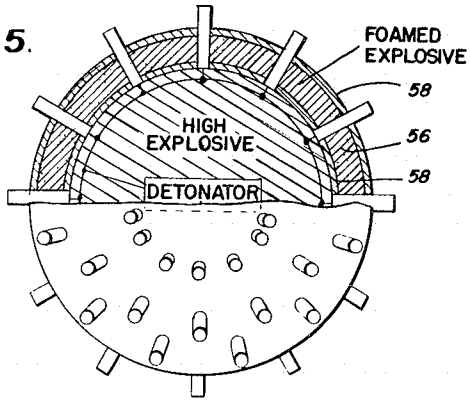


FIG. 8.

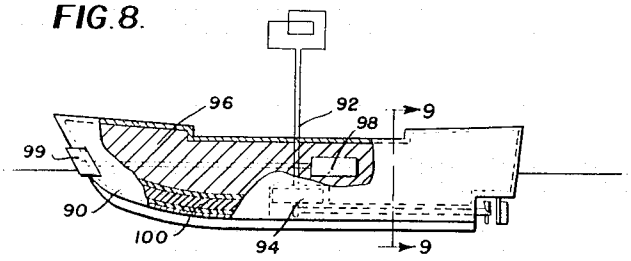
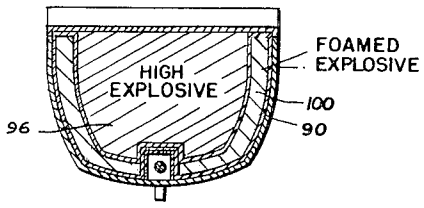


FIG. 9.



INVENTOR.
HOWARD J. STARK
BY George Sipkin
ATTORNEY

United States Patent Office

3,049,454

Patented Aug. 14, 1962

3,049,454

LOW DENSITY CELLULAR EXPLOSIVE FOAM

Howard J. Stark, 920 N. Lebanon St., Arlington, Va.

Original application Aug. 15, 1955, Ser. No. 528,566, now Patent No. 2,768,072, dated Oct. 23, 1956. Divided and this application Apr. 25, 1956, Ser. No. 580,677

6 Claims. (Cl. 149—92)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to low density explosives and in particular to a low density, cellular explosive foam.

This is a related application to claim the subject matter required to be divided out of copending application Serial No. 451,723, filed August 23, 1954, now Patent No. 2,845,025 issued July 29, 1958, and entitled Low Density Cellular Explosive Foam and Products Made Therefrom, and which was a continuation application of then copending and now abandoned application Serial No. 185,900, filed September 20, 1950, and entitled Low Density Cellular Explosive Foam. This is a divisional application of copending application Serial No. 528,566, filed August 15, 1955, now Patent No. 2,768,072 issued October 23, 1956, and entitled Method of Producing a Low Density Explosive which was a continuation-in-part application of then copending and now abandoned application Serial No. 300,367, filed June 30, 1952, and entitled Low Density Cellular Explosive Foam which was a divisional application of Serial No. 185,900, supra.

The general object of the invention is to provide an explosive having a cellular foam structure which, because of such foam structure, is of relatively low density, is buoyant with respect to water, and of greater and more rapid shattering effect than the same weight of high density explosive.

It is also an object of the invention to provide an explosive having a cellular foam structure which is set and rigid and which is relatively strong and tough.

It is a further object of the invention to provide an explosive having a cellular foam structure which may be cast or molded into a particular shape prior to the setting or assumption of rigidity.

Other objectives will be apparent from the following description and from the drawings, hereto attached, which are illustrative of the method of making the cellular explosive and of the preferred embodiments of the invention.

In these drawings:

FIG. 1 is a flow chart of the dynamic air-set method of this invention;

FIG. 2 is a flow chart of the "chemical blowing" method of this invention;

FIG. 3 is a diagrammatic transverse section through a conventional floating mine;

FIG. 4 is a diagrammatic transverse section through a floating mine of the type illustrated by FIG. 3 but containing a relatively large quantity of the foamed explosive of this invention cast in situ;

FIG. 5 is a diagrammatic sectional-elevational view of a floating mine in which the shell is comprised of the molded foamed explosive of this invention encased in light weight metal or impregnated fabric and shows the increased high explosive charge possible with this type of construction;

FIG. 6 is a diagrammatic longitudinal section through a floating, harbor mine showing the combination in the explosive charge of the conventional high density explosive with the foamed explosive of this invention;

FIG. 7 is a diagrammatic longitudinal sectional-elevational view of a torpedo carrying a charge of high density explosive and foamed explosive of this invention; and

FIGS. 8 and 9 are a diagrammatic longitudinal sectional-elevational view and a transverse sectional view taken on line 9—9 of FIG. 8, respectively, of a radio controlled "homing" vessel showing the foamed explosive of this invention cast and molded within the structure of the double walled hull.

Heretofore, it has been the practice, in the manufacture of explosive, to produce them with a relatively high density in order to have a great explosive effect in a given volume. Now a requirement has arisen in which it is desirable to have an explosive which is buoyant and which may have a greater explosive effect which may be additive to that of the conventional high density explosive. This requirement is present not only in floating mine structures, but also in the guided surface (the so-called "homing") vessels.

This inventor has met this requirement by providing a foam type explosive which resembles in physical appearance and characteristics cellular polystyrene or cellular acetate. It is relatively strong and tough and the density thereof can be varied by formulation within the range of from about 5 to about 50 pounds per cubic foot.

The cells of the foamed and set structure of the explosive are substantially non-communicating and referred to as closed-cells in contradistiction to spongy open-cells. Therefore, a molded plate of this material is relatively impervious to gas and water. In comparison with balsa wood, which has a buoyancy of about twenty pounds per cubic foot after twenty-four hours immersion under a ten foot head of water, this cellular explosive has a buoyancy of from about 20 to about 50 pounds per culbic foot under similar conditions.

The following explosives, as well as others, can be prepared in foam or cellular form:

(1) Trinitrotoluene
(2) Nitrocellulose (tri, hexa and dodeca nitrocellulose)
(3) Pentaerythritol
(4) RDX (cyclo triemethylenetrinitramine)

The foamed explosive consists essentially of any one of the above explosives bonded by a foaming plastic.

A foaming plastic is a plastic which will be of solid cellular structure when it is allowed to set after being foamed either by chemically or mechanically blowing gas or air through it while in the liquid stage as will appear in the example set forth below.

This inventor has found that polyesters of ethylene glycol-maleic anhydride intermixed with monomeric styrene is ideally suited as a resin in the carrying out of this invention. This resin is shown and described along with other resins which also are suitable in Carleton Ellis' Patent 2,255,313, which is incorporated by reference and forms a part of this specification. Of course a filler as used in the examples of Ellis is unnecessary and not used although such use would still fall within the scope of what is considered to be the present invention.

An example of one of these resins is that produced by heating 500 parts of maleic anhydride and 541 parts diethylene glycol in an oil bath at 220–225° C. for 7 hours while bubbling nitrogen gas therethrough to provide an inert atmosphere. The diethylene glycol maleate formed is a light-colored viscous liquid of acid number 7.1. Eighty-five parts of this liquid are mixed with 5 parts monomeric styrene in a glass container with a mechanically driven stirrer. The resultant liquid is a satisfactory stock solution and has 3% (by weight) benzol peroxide (curing agent) and 3½% (by weight) cobalt naphthanate (accelerator) added to it just prior to its use.

These bonding thermosetting polyester resins are well known in the field of resin chemistry and their specific compositions form no part of this invention. The requirements thereof are that they be compatible with solutions of the explosives, that they gel at room temperature in a relatively short period of time such as about fifteen minutes, set permanently in about one hour and that they impart a viscosity to the solution of the explosive sufficient to prevent the escape of air therefrom and yet be sufficiently fluid for efficient molding and casting. The rate of setting of these resins is controlled by the addition thereto of a relatively small proportion (from about 2% to about 4% by weight) of an appropriate curing agent. Such agents have been found to include: benzol peroxide, ditertiarybutyl peroxide, cumenehydro peroxide, methylisobutyl ketone peroxide, and dibenzaldeperoxide. The choice of the particular curing agent used depends upon its compatibility with the solution of the resin and the explosive and the rate of curing desired. Also an accelerator, such as cobalt naphthanate may be added in a proportional amount of from about 2% to about 5% by weight to give additional control on the rate of gelling and setting of the resin. These curing agents and accelerators are herein referred to as setting agents.

Commercially available resins which have been found to be suitable as a bond for the foamed explosives of this invention are "MR-28C and 29C" by Marco Chemicals, Inc., "Selectron 5003 and 5016" produced and marketed by the Pittsburgh Plate Glass Company, "Laminac 4128, 4129 and 4116" produced and marketed by the American Cyanamid Company, and "Paraplex P–43" by Rohm and Haas Company.

Two methods of the preparation of foamed explosive are preferred by this inventor. These are (1) the so-called dynamic air-set method, and (2) the chemical blowing method. These methods differ from each other mainly in the method of introduction of air or gas into the resinous solution of the explosive. In the dynamic air-set method (reference being had to FIG. 1 of the drawings), a solution of the explosive in styrene, ether, acetone, or a mixture of some of these or other solvents is made as indicated at **10**. Only as much explosive may be dissolved as will go into the solution with or without the application of a moderate heat, and with staying below the decomposition temperature of the explosive. A solution of a foaming plastic such as polyester type resin, a curing agent or "catalyst" and an accelerator is prepared as shown at **12** in the proportionate amounts above indicated. From about 10 to about 30% by volume of the liquid resin solution is mixed with the solution of the explosive as shown at **14**.

As an example, the diethylene glycol maleate with monomeric styrene is mixed with benzol peroxide and cobalt naphthanate as specifically set forth above. About 20% by volume of this solution is mixed with a saturated solution of TNT dissolved in styrene.

The curing agent and accelerator will cause the resin to gel in about 15 minutes and to set permanently in about one hour. The mixture of solutions of the explosive and resin is stirred for about 5 minutes as indicated at **15** and allowed to rest for about 5 minutes. Compressed air from a source (not shown) is introduced into blowing chamber **18** and thence through foraminous member **20** which may be a glass frit or metal screen of a mesh in the range of from 75 to 300 and through the mixture at **14** for about 3 minutes which will foam the said mixture. The foamed mixture is then poured into molds or other containers within the remaining 2 minutes of the 15 at which time the foamed explosive gels or sets up and in one hour becomes a hard cellular mass. By a proper control of the viscosity of the mixture, above referred to, air bubbles do not appreciably escape therefrom after the completion of the blow or during the period that the mixture is in the mold prior to gelation. There is therefore no collapsing of the foamed structure in the mold.

In the chemical blowing process the explosive is dispersed in a suitable solvent such as acetone or styrene as indicated at **24** in FIG. 2 to obtain a saturated or highly viscous solution. A solution is prepared by the addition of a curing agent and an accelerator to a foaming plastic in the proportionate amounts above indicated and as shown at **26**. The foaming plastic may be a polyester type resin as above described or other foaming plastics set forth below. In either case they are adjusted to gel in about fifteen minutes and to set in about one hour as in the process above described. The solutions of the explosive and the resin are conducted into mixing chamber **28**, the solution of the resin being added in the proportion by volume of from 10% to 30%. In this chamber there is added to the mixture from 10% to 30% by volume of a chemical blowing agent such as diazoaminobenzene or toluene diisocyanate. The mixture is stirred, as indicated at **30** for from five to ten minutes and is then poured or cast into molds as indicated at **32**. The molds are then heated as indicated at **33** to a temperature of about 120° C. but not above decomposition temperature of the explosive at which temperature the blowing agent evolves a relatively large volume of gas which causes the mass to expand forming a cellular structure.

The range in composition, on a percentage weight basis at various temperatures of formation, of the foamed explosives of this invention is given in the following table:

° C. Temp.	Solvent	Percent Range in Comp.	Explosive	Percent Range in Comp.	Percent Range in Comp. of Resin
20	acetone	10	T.N.T	80–60	10–30
20	toluene	40	T.N.T	50–30	10–30
20	benzene	30	T.N.T	60–40	10–30
60	acetone	5–10	T.N.T	85–60	10–30
60	toluene	5–10	T.N.T	85–60	10–30
60	benzene	5–10	T.N.T	85–60	10–30
80	acetone	5	T.N.T	85–65	10–30
20	do	70	PETN	25	5
60	do	50	PETN	40	10
112	toluene	60	PETN	30	10
25	cyclohexanone.	78	RDX	12	10
60	acetone	67	RDX	18	15
97	cyclohexanone.	60	RDX	25	15
25	do	78	HBX–1 & 2	12	10
60	acetone	67	HBX–1 & 2	18	15
97	cyclohexanone.	60	HBX–1 & 2	25	15

Other examples using different foaming plastics are set forth below and it will be understood by a chemist familiar with the art that such foaming plastics are capable of use with the dynamic air-set method as well as the chemical blowing method.

A chemically blown foamed explosive can be prepared by using toluene diisocyanate and alkyd resins to produce a composition referred to in the art as polyurethane foam resins. Carbon dioxide is liberated in the reaction to cause the plastic to foam and thus, in effect, the ingredients act as their own blowing agents.

For purposes of this invention an alkyd resin having following composition is prepared:

7.6 parts by weight glycerol
5.0 parts by weight adipic acid
1.0 part by weight phthalic anhydride

These ingredients are refluxed in a glass lined container in an atmosphere of carbon dioxide and at a temperature of about 165° C. until an acid number of about 55 and hydroxyl number of about 415 are reached. The alkyd resin thus formed is then cooled to room temperature for further use as described below.

Ratios of explosive to resin by weight range from 10% resin to 90% explosive to 50% resin and 50% explosive.

Optimum results are obtained where 10 to 30% of resin is used with 90 to 70% of explosive. The following composition is prepared in the following manner to produce a polyurethane explosive foam:

(A) 150 parts by weight of alkyd resin as prepared above.
(B) 1350 parts by weight of TNT contained in warm acetone (about 30° C.).
(C) 140 parts by weight 2-4 M-toluene diisocyanate.
(D) 58 parts by weight of water.

Ingredients (A) and (B) are first mixed in a mechanical mixer such as a Hobart of suitable capacity. Then ingredient (C) is mixed therewith followed by ingredient (D) which is mixed therewith or stirred for about 20 minutes.

This mixture is then poured into a suitable metal mold calculated to produce the desired density which in this case is about 10 pounds per cubic foot. The closed mold containing the mixture is then placed in a hot air oven at about 73° C. for about one hour after which the mold is removed from the hot air oven and cooled to room temperature and the explosive TNT foam is removed therefrom.

Another example of a manner of practicing the invention, which in this case utilizes a polyvinyl chloride resin with a copolymer of vinyl chloride and vinyl acetate, follows:

About 100 parts of a polymerized material consisting of about 85% by weight of polyvinyl chloride and about 15% by weight of copolymers of vinyl chloride and vinyl acetate are mixed in a Hobart mixer with about 80 parts of tricresyl-phosphate (plasticizer) until the polymer is thoroughly dispersed. About 25 parts of P.P'-oxybis benzene sulfonyl hydrazide (chemical blowing agent) is then added and mixed thoroughly. (Diazoaminiobenzene or 40% dinitroso pentamethylenetriamine may also be used as chemical blowing agents.) About 3 parts of lead stearate (stabilizer) is also added and mixed thoroughly.

About 80 parts by weight of TNT in a fine state of division such as will pass through a Standard Sieve No. 50 or 100 (as defined by the American Society for Testing Materials Standards) is then added to the above composition and the mixture worked to a uniform consistency with a stiff blade mechanical mixer. About 10% by weight of the combined ingredients of acetone is then added slowly and the mass mixed to uniform consistency.

A suitable charge or volume of this product is placed in a steel mold of desired shape. Such an example would be a mold 6" x 6" x ½" of heavy steel wall construction as established in the art or industry for processing these products. The mold cavity is completely filled, and the charged mold placed in between press platens at a temperature of about 160° C. The press is then closed and about 5000 p.s.i. pressure applied to the mold and held for about 20 minutes at this temperature. After this time the pressure is reduced to atmospheric and the mold removed from the press. The mold is opened and the molded piece is removed. It is then placed in a hot air oven or chamber at about 120° C. for about 60 minutes when the piece will then grow or expand to about double its volume producing a density between 4 and 7 pounds per cubic foot. The density can be considerably changed by varying the charge into the mold and the weight of explosive incorporated into the mold.

An epoxy resin can be used in carrying out the invention in a manner such as shown by the specific example below.

About 110 parts of a diphenol such as bisphenol A is dissolved in 80 parts thereof of a 20% water solution of sodium hydroxide. About 188 parts of epichlorohydrin is slowly added to the mixture at about 75° C. over approximately a 30 minute period. The resulting resin melts at about 65° C.

Explosive foam mixture is prepared using the following ingredients:

	Parts
Epoxy resin as above	98.0
Ammonium bicarbonate (blowing agent)	10.0
Diglycol laurate S (wetting agent)	3.5
Piperidine (curing agent)	2.0
TNT	400.0

Epoxy resin as above is heated to the liquid stage at about 75° C. The ammonium bicarbonate previously dispersed in diglycol laurate S is then added and stirred thoroughly. The TNT is then added and stirred, followed by the piperidine which is then added and mixed for about 5 minutes. The liquid phase life at this stage is limited to about 30 minutes; otherwise, polymerization or solidification sets in. The mixture is then transferred to a heated metal mold or box held at about 75° C. for about 2 hours when the explosive foam is made. The explosive completely fills the container. Of course the explosive foam mixtures may also be made from nitrocellulose, pentaerythritol, and cyclo trimethylenetrinitramine. The density of the explosive foam is controlled by varying the percentage of explosive going into the composition and the weight of mix going into the heated mold cavity or box as described above.

This particular explosive foam composition may also be cured using other amine reagents such as diamines, triamines or quaternary amines such as, diethylenetriamine and triethylenetetramine. Commercial resins such as Shell Chemical Company "Epon" resins such as "Epon 834, Epon 864, and Epon 1001" and mixtures of these various resins may also be used. Cure or hardening is accomplished by using any one of the amines stated above.

Referring further to the drawings, in FIG. 3 a conventional floating mine is shown diagrammatically and generally at **40**. The mine comprises a metallic case **42**, contact elements **44** which are in electric circuits **46** with the detonating or exploding device **48**. This exploding device detonates the charge of high explosive **50** when any one of the elements **44** is actuated by contact with an object in the water. The interior volume of this type of mine is comprised of about 50% air space as shown at **52**.

In FIG. 4 the air space of the mine shown in FIG. 3 is filled with the foamed explosive of this invention as shown at **54** which has been cured and set in place. This foamed or cellular explosive not only gives an additive effect to the "brisance" of the high explosive, but in the event of leakage through metallic shell **42** due to erosion or corrosion thereof, the buoyancy of the mine will be maintained substantially as that existing when the mine is in leakproof condition.

FIG. 5 is illustrative of an embodiment of this invention in which the shell of the mine is comprised of molded cellular explosive **56** covered on the exterior and interior faces with a relatively thin layer of metal or impregnated fabric **58**. The increased buoyancy of this type of construction over the conventional, heavy metallic case mine is readily apparent. In fact, the buoyancy is so much greater that substantially the entire interior space of the mine may be filled with high density explosive thereby producing a mine of greatly increased shattering effect when also considered in the light of the additive explosive effect of the cellular explosive comprising the shell.

FIG. 6 is a sectional illustration of a floating harbor mine showing the arrangement of a metallic casing **60**, a high density explosive charge **62**, detonating or exploder device **64**, actuating contact element **66** and foamed explosive of this invention **68** surrounding the high explosive charge and exploder device and filling the air space normally present within the casing of this type of mine. In the event of leakage of water through the casing due to corrosion thereof or otherwise, the foamed explosive prevents loss of buoyancy and the normally resultant loss of the mine.

FIG. 7 is a sectional-elevational view of a torpedo shown generally at **70** in which the foamed explosive **72**

of this invention fills the normally present air-space within the shell **74**. The legends in this figure are believed to be self-explanatory. In this embodiment of the invention, the overall buoyancy of the torpedo is less than that of the torpedo having the conventional air space. But the total shattering effect of the explosion is much increased by this additional quantity of foamed high explosive. In charging this cellular explosive into this air space in the torpedo, the foamed explosive is poured into this space immediately prior to the gelling thereof. The space is completely filled and upon the curing and setting of the resin component the cellular explosive becomes rigid and reinforces the sidewalls of the shell.

FIGS. 8 and 9 show the application of the foamed high explosive of this invention to the structure of an electronically controlled homing vessel in sectional-elevational views. Here the double walled hull **90** is shown provided with radio control **92** for motor drive mechanism **94**. High density high explosive **96** substantially fills the interior of hull **90** surrounding the exploder device **98**. The detonating contact element is shown at **99**. The space within the double wall structure of the hull is filled with the foamed high explosive of this invention as shown at **100**. As in the case of the torpedo above-described, the foamed explosive is poured into this hull wall spaced immediately prior to the gelling and after setting the foamed cellular explosive mechanically reinforces the structure. The advantage of this type of construction of these homing vessels is that the shattering effect of the explosion is greatly increased and that in the event of leakage through the outer wall of the hull due to corrosion or to any other cause the buoyancy of the vessel is maintained.

It should be understood, of course, that the foregoing disclosure relates to only preferred embodiments of the invention and that it is intended to cover all changes and modifications of the examples herein chosen for the purposes of the disclosure, which do not constitute departures from the spirit and scope of the invention as set forth in the appended claims.

I claim:

1. An explosive whose density is less than that of water which comprises a foam wherein substantially all the cells are closed and impervious to the passage of fluid, said foam being a homogeneous mixture of about 90 percent to about 70 percent by weight of an explosive from the group consisting of trinitrotoluene, nitrocellulose, pentaerythritol, and cyclo trimethylenetrinitramine and a binder of about 10 percent to about 30 percent by weight of a thermosetting polyester resin.

2. An explosive whose density is less than that of water which comprises a foam wherein substantially all the cells are closed and are impervious to the passage of fluid, said foam being a homogeneous mixture of about 88 percent to about 67 percent by weight of trinitrotoluene and from about 12 percent to about 33 percent by weight of a thermosetting bonding polyester resin.

3. An explosive whose density is less than that of water which comprises a foam wherein substantially all the cells are closed and are impervious to the passage of fluid, said foam being a homogeneous mixture of about 85 percent to about 60 percent by weight of nitrocellulose and from about 15 percent to about 40 percent by weight of a thermosetting bonding polyester resin.

4. An explosive whose density is less than that of water which comprises a foam wherein substantially all the cells are closed and are impervious to the passage of fluid, said foam being a homogeneous mixture of about 85 percent to about 75 percent by weight of pentaerythritol and from about 15 percent to about 25 percent by weight of a thermosetting bonding polyester resin.

5. An explosive whose density is less than that of water which comprises a foam wherein substantially all the cells are closed and are impervious to the passage of fluid, said foam being a homogeneous mixture of about 65 percent to about 55 percent by weight of cyclo trimethylenetrinitramine and from about 35 percent to about 45 percent by weight of a thermosetting bonding polyester resin.

6. An explosive whose density is less than that of water which comprises a foam wherein substantially all the cells are closed and impervious to the passage of fluid said foam being a homogeneous mixture of about 90 percent to about 70 percent by weight of trinitrotoluene and from about 10 percent to 30 percent of an alkyd resin.

References Cited in the file of this patent

UNITED STATES PATENTS

2,062,011	Norman	Nov. 24, 1936
2,165,263	Holm	July 11, 1939
2,171,379	Wahl	Aug. 29, 1939
2,334,149	Ripper	Nov. 9, 1943
2,349,048	Mackey	May 16, 1944

FOREIGN PATENTS

674,447	Great Britain	June 25, 1952