Jan. 15, 1957 R. W. LAWRENCE 2,777,389

INITIATING DEVICE AND METHOD OF MANUFACTURE

Filed June 13, 1952

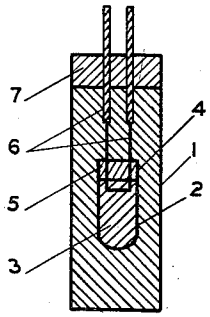


FIG. 1

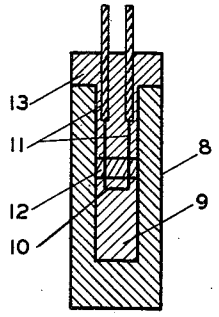


FIG. 2

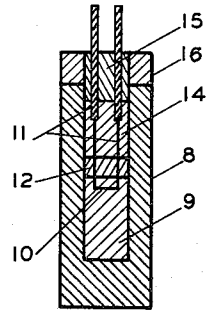


FIG. 3

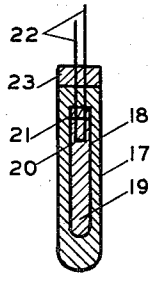


FIG. 4

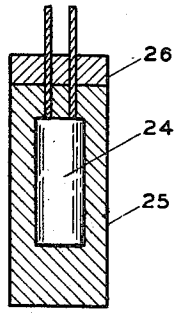


FIG. 5

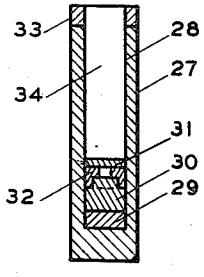


FIG. 6

Robert W. Lawrence

INVENTOR.

BY Ernest G. Peterson

AGENT.

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INITIATING DEVICE AND METHOD OF MANUFACTURE

Robert W. Lawrence, Wilmington, Del., assignor to Hercules Powder Company, Wilmington, Del., a corporation of Delaware

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8 Claims. (Cl. 102—28)

This invention relates to initiating devices for explosives and more particularly to a blasting cap and method of producing same in which the main explosive charge is an explosive-plastic composition in which the initiating components are disposed and which eliminates the necessity for providing a separate shell.

At present all commercial electric blasting caps are essentially prepared by pressing a base charge into a metallic shell, adding a loose or pressed initiating charge, inserting a bridge wire or matchhead ignition assembly, adding a waterproofing compound, and finally sealing the cap with sulfur. In some methods the last two steps have been eliminated by employing a plastic or rubber plug in the ignition assembly to seal the cap. Other methods include the use of shells of molded organic plastic having disposed therein an explosive charge composed of a series of preformed tablets of high explosive. This last method of manufacture has found little commercial success although plastic plugs may be used which are compatible with the shell and which may be effectively bonded thereto by solvent.

In accordance with the known methods of manufacture, the shell of prior art detonators has merely functioned as a structural requisite and has been inert as far as the development of a detonative force is concerned. While it has been known to enclose a squib in a combustible container, in any of the prior art detonators it is the base charge within the shell which is detonated. The shell has been inert and has not contributed directly to the explosive force generated by the exploding detonator.

Thus, it is a principal object of this invention to produce an initiating device which eliminates the nonexplosive shell heretofore deemed necessary. It is a further object of this invention to produce an explosive mixture that will serve as base charge and waterproof container for the initiating charge.

It is a still further object of this invention to provide safer and more water-resistant detonators at a reduced cost.

Other objects of this invention will be apparent hereinafter as set forth in the specification and appended claims.

Generally described, the present invention comprises an initiating device or blasting cap and a method of producing same in which the device has an explosive waterproof outer shell or main explosive charge comprising a thermoplastic or thermosetting waterproof resinous polymerization product having dispersd therein from about 55% to about 85% of detonative, crystalline high explosive having an average oxygen balance of not less than about —47. The explosive polymerization product forming the shell is formed by in situ polymerization of a polymerizable material containing the particulate explosive.

The polymerizable substances which are operable as starting materials in preparing the explosive polymerization products of the invention are those which form thermoplastic or thermosetting polymerization products without evolving gaseous or liquid by-products. Since the formation of such by-products is detrimental to the

strength, appearance, and moisture resistance of the plastic bodies, condensation products and starting materials which form condensation products are inoperative in the invention. The explosive component of the polymerization product may be a single explosive having the requisite oxygen balance or a mixture of such explosives. If desired, a mixture of one or more crystalline high explosives of varying oxygen balances may be employed as long as the mixture has an oxygen balance of at least —47.

Also included in the invention is a process for manufacturing such detonating devices which comprises admixing particulate, detonative, crystalline high explosive having an average oxygen balance of not less than —47 with a flowable, catalyzed, polymerizable material, supporting the resulting mixture in form of a shell with a cavity therein for containing an initiating element such as by introducing the same into a mold, curing the mixture at a temperature not greater than about 100° C. until a solid polymerization product is obtained, and disposing an initiating element in the polymerization product. The ignition element may also be disposed in the mixture within the mold prior to curing. In addition, a conventional cap may be disposed within a polymerizable mixture and the mixture cured around the cap.

Preferred embodiments of the invention have been chosen for purposes of illustration and description and are shown in the accompanying drawing wherein reference symbols refer to like parts wherever they occur.

Fig. 1 is a sectional view of one form of initiating device in which the main explosive charge is molded in situ around the initiating unit.

Fig. 2 is a sectional view of another form of initiating device in which the main explosive charge is molded with a cavity in which the initiating components are subsequently placed and the cap sealed with a synthetic resin after insertion of the electrical bridge assembly.

Fig. 3 is a sectional view of still another form of initiating device similar to that in Fig. 2 except that it is sealed with an asphaltic waterproofing compound and sulfur respectively.

Fig. 4 is a sectional view of still another form of initiating device in which the initiating components are molded in situ within a small diameter explosive shell.

Fig. 5 is a sectional view of still another form of initiating device in which a regular electric blasting cap is disposed in an explosive polymerization product.

Fig. 6 is a sectional view of still another form of initiating device in which the initiating components are disposed within the main explosive charge provided with a cavity adapted to receive a fuse.

In Fig. 1, the initiating device has a main explosive charge 1 of molded explosive synthetic resin. Within the charge 1, there is disposed a capsule 2 which contains a priming charge 3, a bridge wire 4, and a plug 5. The primer charge 3 is in operative contact with the high explosive of charge 1 to cause detonation of the said explosive in response to heat developed by flow of current through bridge wire 4. A pair of leg wires 6 connected to the bridge wire 4 extends through the plug 5 and charge 1 in conventional manner for connection to a source of electrical energy for firing the device. A collar 7 of nonexplosive synthetic resin is cast and polymerized in situ with the main charge 1 and is thereby bonded to it to complete the initiating device.

In Fig. 2 the initiating device has a main explosive charge 8 of molded explosive synthetic resin. The charge 8 is molded having a well or deep longitudinal cavity and is polymerized in this form. A priming charge 9 is placed in the shell and a bridge plug assembly is pressed thereon. The bridge plug assembly consists of a bridge wire 10 connected to a pair of leg wires 11 which extends through a plug 12. A seal 13 of nonexplosive resin, which

surrounds the leg wires 11, fills the remaining portion of the cavity and forms a collar, is then cast and cured to complete the initiating device.

In Fig. 3, the initiating device is produced similar to that illustrated in Fig. 2. However, in lieu of the seal 13, there is provided an asphaltic waterproofing compound 14 and a sulfur seal 15 which together surround the leg wires 11 and completely fill the cavity. A collar 16 of nonexplosive resin is molded or cast prior to the curing of the main explosive charge and is polymerized therewith to give a good bond. The hard upper surface of the devices as provided by the collars 7 and 16 or seal 13 of nonexplosive synthetic resin is desirable to eliminate any possibility of chipping during insertion of the caps in relatively hard explosive compositions.

If additional explosive content is desired for the device, explosive synthetic resin may also be utilized for sealing or the collar or both. In this case for constructions such as shown in Figs. 2 and 3, the added explosive resin would be cured in a second curing operation or after a partial curing of the main charge.

In Fig. 4, the initiating device, more particularly an electric blasting cap, has a main explosive charge or shell 17 of molded explosive synthetic resin. This cap is of small diameter in the order of 0.27 inch thereby simulating a commercial No. 6 blasting cap with the exception of being shorter in length since the explosive composition comprising the shell serves as the base or main charge. Within the shell 17, there is disposed a capsule 18 which contains a priming charge 19, a bridge wire 20, and a plug or wrapping 21 to hold the leg wires 22 in place. The leg wires 22 are connected to the bridge wire 20 in the usual manner. A collar 23 of nonexplosive synthetic resin is cast or molded and polymerized in situ with the main charge to complete the cap.

In Fig. 5, the initiating device is produced similar to that illustrated in Fig. 1 with the exception that a regular electric blasting cap 24 is disposed within a molded explosive synthetic resin 25. This type of initiating device provided with means to increase the initiating propensity of the device is commonly referred to as a booster cap and is used in conjunction with insensitive explosives.

In Fig. 6, the initiating device, more particularly a fuse type blasting cap, has a main explosive charge or shell 27 of molded explosive synthetic resin. Within the shell 27, there is disposed a capsule 28 which contains a base charge 29, initiating charge 30, and a wafer charge 31. The initiating charge 30 is pressed under a perforated capsule 32 and the wafer charge 31 is pressed thereabove. A collar 33 of nonexplosive synthetic resin is cast or molded and polymerized in situ with the main charge to complete the cap. The longitudinal cavity 34 provided in the cap is adapted to snugly receive a fuse, such as a black powder fuse, for initiation of the cap.

Although the blasting caps depicted are cylindrical, other configurations may be utilized. This may be done to accommodate certain desired ignition assemblies such as the cavity plug or matchhead types or may be done to facilitate insertion into explosive charges. Thus, the blasting caps need not be molded to a constant radius but may be various shapes such as tapering at the bottom, or top and bottom, flat in cross section, etc. Generally, however, extremely sharp edges are to be avoided to prevent possible fracture of the shell material at such junctions.

The following examples illustrate various methods of carrying the invention into effect.

Example 1

A benzoyl peroxide (0.006 g.) catalyst was dissolved in 3 g. of methyl methacrylate monomer, and 10 g. of PETN added to the solution. The mixture was stirred until the PETN was thoroughly wet and then placed in a 0.5-inch glass vial. The mixture was packed down lightly with a ½-inch brass rod, taking care to wet the vial sidewalls thoroughly to displace air bubbles. A 0.25-inch rod wrapped in 0.0005-inch thick aluminum foil and centered in a small cork was inserted into the mixture to within ¼ inch of the bottom, the cork fitting snugly on the neck of the vial. The vial was sealed with a screw lid and placed in an oven at 50° C. The sample was removed after 16 hours and allowed to cool, after which the sample was freed, and the center rod removed. First, 0.1 g. PETN was placed loosely into the 0.25-inch cavity, and then 0.3 g. diazodinitrophenol placed on top of the PETN. A bridge wire assembly was then placed on the diazo and the cavity sealed with molten sulfur. Upon the passage of current through the bridge wire, the device detonated completely.

Example 2

A benzoyl peroxide (0.006 g.) catalyst was dissolved in 3 g. styrene, and 10 g. of PETN added to the solution. The mixture was stirred until the PETN was thoroughly wet and then placed in a 0.5-inch glass vial. The mixture was packed down lightly with a ½-inch brass rod, taking care to wet the vial sidewalls thoroughly. A 0.25-inch rod wrapped in 0.0005-inch thick aluminum foil and centered in a small cork was inserted into the mixture to within ¼ inch of the bottom, the cork fitting snugly on the neck of the vial. The vial was sealed with a screw lid and placed in an oven at 50° C. The sample was removed after one week and allowed to cool, after which the sample was freed, and the center rod removed. First, 0.1 g. PETN was placed loosely into the 0.25-inch cavity, and then 0.3 g. diazodinitrophenol placed on top of the PETN. A bridge wire assembly was then placed on the diazo and the cavity sealed with molten sulfur. Upon the passage of current through the bridge wire, the device detonated completely.

Example 3

Ten grams of PETN was mixed with 3 g. of a styrene/polyester resin following which 0.03 g. of tertiary butyl hydroperoxide was mixed in. This mixture was pressed in increments into a ⅝-inch inside diameter glass tube which was coated with a mold-release compound containing carnauba wax. After this was well tamped into the mold, an electric blasting cap 0.27-inch O. D. and 1⅛ inches long, and sealed with a Bakelite plug, was pressed in so that the bottom of the electric blasting cap was ½ inch above the bottom of the mold. One-half inch of the clear resin was poured in on top of the explosive composition. The molded composition was then placed in an oven at 50° C. for 18 hours. The mold was then cooled, and the cured plastic cap was removed from the mold. The resulting cap was placed on a 3/16-inch steel plate and detonated. It produced a hole 12 mm. in diameter.

Example 4

An initiating device was prepared in accordance with the procedure of Example 3 with the exception that cyclonite was added to the solution in place of PETN. Upon the passage of current through the bridge wire, the device detonated completely.

Example 5

An initiating device was prepared in accordance with the procedure of Example 3 with the exception that sucrose octanitrate was added to the solution in place of PETN. This device was placed against a 3/16-inch steel plate and upon the passage of current through the bridge wire the device detonated completely producing a hole through the plate.

Example 6

An initiating device was prepared in accordance with the procedure of Example 3 with the exception that man-

nitol hexanitrate was added to the solution in place of PETN. This device was placed against a 3/16-inch steel plate and upon the passage of current through the bridge wire the device detonated completely producing a hole through the plate.

Example 7

An initiating device was prepared in accordance with the procedure of Example 3 with the exception that tetryl was added to the solution in place of PETN. This device was placed against a 3/16-inch steel plate and upon the passage of current through the bridge wire the device detonated completely producing a hole through the plate.

Example 8

An initiating device was prepared in accordance with the procedure of Example 3 with the exception that lactose octanitrate was added to the solution in place of PETN. This device was placed against a 3/16-inch steel plate and upon the passage of current through the bridge wire the device detonated completely producing a hole through the plate.

Example 9

A benzoyl peroxide (0.006 g.) catalyst was dissolved in 3 g. of glycol and toluene diisocyanate mixture. In preparing the mixture, 3 g. of an equimolar mixture of ethylene glycol and toluene diisocyanate was shaken together until a homogeneous solution was obtained. The catalyst containing solution was then mixed with 10 g. of PETN, charged into a glass mold, an electric blasting cap was embedded in the plastic mix, and then cured for two hours at 50° C. after which the finished device was removed from the mold. When this device was shot against a 3/16-inch steel plate, a hole ½ inch in diameter was made through the plate.

Example 10

A benzoyl peroxide catalyst (0.006 g.) was dissolved in 3 g. methyl methacrylate monomer, and 10 g. of PETN added to the solution. The ingredients were stirred until the PETN was thoroughly wet and then placed in a 0.5-inch glass vial. The mixture was packed down with a ½-inch rod, taking care to wet the vial sidewalls thoroughly. Two grams of methyl methacrylate monomer containing 0.004 g. benzoyl peroxide was then poured on top of PETN-methyl methacrylate mixture. Loose PETN (0.05 g.) was placed in a No. 1 gelatin capsule (0.25-inch diameter) and 0.25 g. diazodinitrophenol placed on top of that. The capsule was then forced onto a 0.25-inch Bakelite bridge wire assembly plug. The lead wires were run through a rubber stopper, and then the capsule embedded in the monomer-explosive charge, the rubber stopper being forced into the neck of the vial. The sample was placed in an oven at 50° C. for 16 hours. The cured charge was removed from the vial. Upon the passage of current through the bridge wire, the cap detonated completely.

Example 11

A benzoyl peroxide catalyst (0.006 g.) was dissolved in 3 g. of methyl methacrylate monomer, and 10 g. of PETN added to the solution. The ingredients were stirred until the PETN was thoroughly wet, and then 2 g. of the mixture placed into a glass tube, 0.30 inch by 2 inches long. The mixture was packed down with a 0.22-inch rod, taking care to wet the tube sidewalls. An additional gram of methyl methacrylate monomer (containing 0.002 g. benzoyl peroxide) was then poured on top. A 0.22-inch rod wrapped in 0.005-inch aluminum foil and centered in a cork was inserted into the mixture, the cork sealing the tube. The tube was placed in an oven at 50° C. for 16 hours. The sample was then removed, cooled, and the charge freed from the tube. The center rod was removed and the cavity charged with 0.05 g. loose PETN and 0.25 g. diazodinitrophenol. A bridge wire assembly was then placed on the diazo, and the cavity sealed with molten sulfur. Upon the passage of current through the bridge wire, the cap detonated completely.

Example 12

A mixture of PETN and styrene/polyester resin in proportion of 77/23 by weight was thoroughly mixed. Tertiary butyl hydroperoxide equal to 1% of the resin content was then mixed in. Then 0.5 g. of the mixture was pressed into a glass mold 0.27 inch inside diameter. A gelatin capsule 0.18 inch inside diameter, containing 0.20 g. PETN and 0.20 g. of diazodinitrophenol, and closed with a Bakelite plug bridge assembly, was embedded in the mixture, so that the bottom of the gelatin capsule was ¼ inch from the bottom of the main charge. Enough clear styrene/polyester resin was added to cover the top of the Bakelite plug to a depth of ¼ inch. The assembly was placed in an oven at 50° C., and heated for about 15 hours to cure the resin. The cap was chilled and removed from the mold. When the cap was shot, by passing an electric current through the bridge wire, it detonated completely.

Example 13

A mixture of 0.5 g. of PETN and 0.5 g. of methyl methacrylate monomer containing 0.2% benzoyl peroxide catalyst were mixed together and charged into a 0.30-inch diameter glass mold. A 0.18-inch gelatin capsule, into which 0.10 g. of PETN had been pressed tightly and 0.10 g. of loose diazodinitrophenol had been added, and a Bakelite plug bridge wire assembly inserted, was then pressed into the methacrylate PETN mixture until the bottom of the capsule was ¼ inch from the bottom of the mold. The PETN in this case settles to the bottom of the very low viscosity methyl methacrylate monomer to give approximately 80% of PETN when gelled, leaving a clear polymer collar on top. The mold was closed with a cork stopper, and the mixture was cured for 24 hours at 60° C. After removing the finished cap from the mold, the cap was detonated by passing electric current through the bridge wire, and it shot completely.

Example 14

An electric blasting cap was prepared in accordance with the procedure of Example 13 with the exception that cyclonite was added to the methyl methacrylate monomer containing catalyst in place of PETN and a mixture of diazodinitrophenol/potassium chlorate 75/25 by weight was used in place of the straight diazodinitrophenol in the primer. After removing the finished cap from the mold, the cap was detonated by passing electric current through the bridge wire and it shot completely.

Example 15

A mixture of PETN and styrene/polyester resin containing 1% of tertiary butyl hydroperoxide was mixed in 77/23 by weight ratio, and packed into a flat-bottomed glass mold in quantity to give a 0.5 g. PETN charge 0.31 inch diameter. Then a 0.18-inch I. D. gelatin capsule about ⅞ inch long was charged with 0.125 g. PETN and 0.100 g. of diazodinitrophenol, each lightly pressed. A Bakelite plug bridge assembly was then friction-fitted into the gelatin capsule so that the bridge wire was in good contact with the diazodinitrophenol. This assembly was then pressed into the PETN resin base charge to within ¼ inch of the bottom. Then additional liquid resin was added to bring the total length to 1¼ inches and seal the charge. The cap was heated at 50° C. for 18 hours to cure the resin. After removing the cap from the mold, it was detonated against a ⅛-inch lead plate and produced a 10-mm. diameter hole.

Example 16

An electric blasting cap was prepared in accordance with the procedure of Example 15 with the exception that

cyclonite was added to the styrene/polyester liquid resin containing catalyst in place of PETN. After removing the finished cap from the mold, the cap was detonated by passing electric current through the bridge wire and it shot completely.

Example 17

A mixture of lead azide and styrene/polyester resin in proportion of 77/23 by weight was prepared and 1% of tertiary butyl hydroperoxide catalyst based on the resin content was mixed therein. This mixture was then charged into a 0.62-inch diameter glass mold, and a copper-acetylide matchhead ignition assembly was embedded in the explosive/resin mixture. Curing of the resin was carried out at 50° C. for 20 hours. When an electric current was passed through the bridge wire of the finished cap, the charge detonated completely.

Example 18

An electric blasting cap was prepared in accordance with the procedure of Example 17 with the exception that a cavity-type ignition assembly was used in place of the matchhead-type assembly. In this embodiment the cavity around the bridge wire was filled with a mixture comprising diazodinitrophenol and potassium chlorate 75/25 by weight prepared in liquid dispersion and then dried. This cavity-type ignition assembly was then inserted into the explosive/resin mixture containing catalyst and cured. When an electric current was passed through the bridge wire of the finished cap, the charge detonated completely.

Example 19

A fuse-type blasting cap was made by placing 0.65 g. of a mixture of PETN and styrene/polyester resin in proportion of 77/23 by weight and containing tertiary butyl hydroperoxide equal to 1% of the resin content in a 0.30-inch glass mold. A 0.22-inch diameter gelatin capsule 2 inches long was pressed into the plastic mixture, so that the bottom of the capsule was ¼ inch from the bottom of the cap. Clear resin was poured on top of the explosive charge in the annular space between the capsule and mold. The resin was then cured in an oven at 50° C. for 18 hours. A charge of 0.1 g. of PETN was placed in the bottom of the gelatin capsule, and then 0.30 g. of diazodinitrophenol pressed under a perforated copper capsule, and then 0.05 g. of diazodinitrophenol was pressed on top of the capsule as a wafer charge. A black powder fuse was inserted into the snugly-fitting plastic shell until it was tight against the explosive charge. The cap was placed against a ⅛-inch lead plate, and ignited by the fuse. It detonated completely, punching a 10-mm. diameter hole through the lead plate.

With reference to the above examples, it is seen that initiating devices or blasting caps may be produced by disposing the initiating components within the main charge either prior to or subsequent to the polymerization reaction.

When the initiating components are disposed within the mold prior to polymerization, it is desirable to provide a capsule for the assembly. The capsule may be made of any material which is insoluble in the polymerizable synthetic resin, which is preferably not an inhibitor therefor, and which can be fabricated with a thin wall. Materials such as gelatin, nylon, aluminum, and copper are acceptable for this purpose although the latter material is the least desirable since it tends to inhibit curing of some synthetic resins. Similarly, the plug material for the bridge wire assembly and the leg wire insulation should be insoluble and preferably free from inhibiting effects when placed in contact with the uncured resin. Materials such as those synthetic resins which do not swell or become brittle as a result of being subjected to the polymerization reaction are preferred, although conventional materials such as sulfur for the plug and cotton yarn for the insulation may be used. Sulfur plugs coming in contact with the resin during polymerization may be coated with lacquer if necessary to prevent undesirable inhibition of the polymerization reaction.

The present invention affords a wide selection of initiating charges and initiating assemblies. Generally, the charges and assemblies used in conventional initiating devices will be found satisfactory or may be rendered so with slight modification. However, in order to insure greater certainty of detonation of the explosive polymerization product constituting the main charge, it is preferred to lightly press into the cavity or the capsule of the main charge from about 0.1 to about 0.2 g. of PETN. This is used in conjunction with initiating explosive such as diazodinitrophenol; diazodinitrophenol/potassium chlorate, for example, a 75/25 mixture; mercury fulminate; mercury fulminate/potassium chlorate, for example, an 80/20 mixture; or a wafer charge of lead azide in combination with an ignition mixture. The ignition mixture may include materials such as lead sulfocyanate; potassium chlorate and ground smokeless powder; or lead/selenium, for example, a 70/30 mixture. Explosive materials other than PETN which may also be used when combined with suitable initiating explosive include cyclonite; PETN/lead azide, for example, 60/40 mixture; sucrose octanitrate; lactose octanitrate; tetryl; etc.

The thermoplastic or thermosetting polymerization products utilized in accordance with this invention may be obtained from suitable monomers, polymers, copolymers, or mixtures thereof. The consistency of the polymerizable materials may vary from very fluid to pasty and the viscosity of these materials may be varied by mixture or by partial polymerization before use. Generally, the materials for the polymerization reaction will be nonexplosive. However, explosive monomers may be employed and explosive materials may be added to the nonexplosive materials for the polymerization reaction providing that the material itself and the amount present do not undesirably inhibit the polymerization reaction. Compounds, such as nitroglycerin, for example, may be incorporated with the resins with which they are compatible to provide additional fuel for the explosive composition as well as adjustment of the viscosity.

More specifically, the originating materials for the polymerization product may be monomeric materials such as the acrylates and diacrylates, the methacrylates and dimethacrylates, styrene, acrylonitrile, diallyl phthalate, and the like. The thermoplastic or thermosetting polymerization products may also be prepared from copolymerizing one or more monomers such as those listed or by copolymerizing such monomers with materials which will cross link. Examples of such mixtures are styrene-glycol maleate, diallyl phthalate-glycol maleate, diallyl phthalate-styrene, Bisphenol epichlorhydrin-dibasic acid, Bisphenol epichlorhydrin-allyl glycidyl ether-dibasic acid, glycol-diisocyanate, acrylic or methacrylic ester-allyl diglycol carbonate or allyl diglycol maleate, and the like.

As previously indicated, the viscosity of the polymerizable material-explosive mixture should be such that it can be readily introduced into molds. Since the operable polymerizable materials cover a wide range of physical characteristics, mixtures of required viscosity can be obtained by blending various of the materials as desired. Viscosity characteristics of the moldable mixtures can also be controlled by the temperature at which they are maintained. If desired, polymerizable mixtures may be formed from polymerizable materials which by themselves cure to thermoplastic compounds and polymerizable materials which by themselves cure to thermosetting compounds. Polymerization products of such mixtures tend to be thermosetting but will soften somewhat on heating. All these materials may be polymerized in situ and have excellent casting characteristics with a cure rate adjustable over a wide range of temperature and time. Moreover, the polymerization reaction of these materials may be carried out under conditions of temperature and catalysis with a temperature of not more than about 100°

C. and in most cases in the range of 50–60° C. or even room temperature, if desired, by proper selection of resin and catalyst. The reactions involved are addition reactions and do not evolve objectionable by-products. As previously indicated, condensation products such as the urea-formaldehyde, resorcinol, and phenolic resins are unsatisfactory for in situ polymerization in accordance with the invention since the by-products formed cause fissuring, cracking, and bubbling.

The preferred catalysts are peroxidic catalysts such as benzoyl peroxide, lauroyl peroxide, and tertiary butyl hydroperoxide. Catalysts such as di-tert-butyl diperphthalate and tert-butyl perbenzoate may be used. The catalysts may be used in conjunction with accelerators or promoters if desired. The cure time of these materials will vary from a few minutes to several days and the amount of catalyst will generally be in the range of 0.2–1.0% by weight of the polymerization product depending on the particular resin used and cure time desired. Especially good results have been obtained with tertiary butyl hydroperoxide and benzoyl peroxide.

The explosive material utilized with the polymerizable material may be selected from a variety of known crystalline, detonative, high explosives providing the explosive is in particulate form or is capable of being reduced to particulate form to insure satisfactory workability. As already indicated, either a single explosive or a mixture of such explosives may be employed as long as the single explosive or mixture has an oxygen balance not less positive than —47. Crystalline explosives having an oxygen balance less positive than —47 can be employed in admixture with crystalline explosives having an oxygen balance above —47 in proportions which will result in the requisite oxygen balance. Explosives such as pentaerythritol tetranitrate (PETN), cyclotrimethylene trinitramine (cyclonite), mannitol hexanitrate, sucrose octanitrate, lactose octanitrate, tetryl and lead azide, and the like, may be used. In the selection of explosives it is desirable to select materials which do not substantially inhibit the formation of the polymerization product. Actually, care need only be taken if TNT (trinitrotoluene) is employed. TNT has an oxygen balance below —47 and therefore will only be employed in admixture with other explosives such as PETN. Even if no care is taken with TNT, an operable casting is obtained although cure time and temperature are increased. If it is desired to use TNT more catalyst should be employed to lower cure time and temperature and a resin or resin mixture should be employed, the polymerization of which is least affected. This also applies to adjuncts such as components molded in situ and the molds or supporting body utilized. Copper and its salts, phenolic bodies and antioxidants are typical of the substances in whose presence proper curing may be more difficult. Atmospheric oxygen may also inhibit polymerization to some extent but these difficulties are obviated by proper choice of resin, catalyst, and curing conditions. The amount of explosive material which may be present is dependent on the characteristics desired of the composition.

The percentage of PETN or cyclonite or equivalent explosive in the main charge of the large initiating devices or caps may be as low as 55% by weight of the explosive polymerization product, although more than 65% is preferable. In the small blasting caps more than 70%, and preferably from about 75 to about 80% by weight of the explosive polymerization product has been found to give excellent results. Furthermore, it has been found preferable to have at least 15% by weight of resin present in the explosive polymerization product to insure adequate structural strength in the end product.

In accordance with the present invention, there is provided efficient blasting caps or initiators affording economies in manufacture. These economies are realized by elimination of the shell and simplification of manufacturing operations. The advantages in use of the devices of this invention principally include elimination of accidental electrical discharge as caused by electrical discharge from the metal casing to the bridge or leg wires through the sensitive ignition explosive, elimination of flying fragments of metal shells which constitute a source of danger and which are undesirable in the mining of certain products, and the ability to perform satisfactorily under water pressure. Thus, the initiators in accordance with this invention may be used where commercial blasting caps, extra strength caps, or booster caps or charges are normally employed. Although the examples and description have been directed primarily to electric blasting caps of the instantaneous type, this is not to be considered as limitative since variations may be made within the spirit and scope of the invention in the production of fuse caps, delay caps, and other detonating devices employing a variety of ignition assemblies including the matchhead and the cavity types.

This application is a continuation-in-part of my copending application Serial No. 25,898, filed May 8, 1948, now abandoned.

What I claim and desire to protect by Letters Patent is:

1. A blasting cap comprising a detonatable explosive waterproof outer shell containing a cavity and comprising a unitary mass of from about 15 to about 45% of a fissure-free synthetic waterproof resinous polymerization product containing dispersed therein from 55–85% of a particulate crystalline high explosive having an oxygen balance of not less than about —47; an initiator means in said cavity which comprises an electric resistance wire, and a pair of lead wires connected with the said resistance wire to convey flow of electric current therethrough from a source of electric current outside said shell; and a primer composition in said cavity in communication with said resistance wire and adapted in operative contact with said high explosive to cause detonation of same in response to heat developed by the flow of current through said wire.

2. A detonating device in accordance with claim 1 in which the particulate explosive is pentaerythritol tetranitrate.

3. A detonating device in accordance with claim 1 in which the particulate explosive is cyclonite.

4. A detonating device in accordance with claim 1 in which the polymer is polymethyl methacrylate.

5. A detonating device in accordance with claim 1 in which the polymer is a styrene polyester.

6. A detonating device in accordance with claim 1 in which the polymer is a polymerized mixture of glycol and toluene diisocyanate.

7. A process for manufacturing a detonating device which comprises admixing polymerization catalyst with fluid monomeric material polymerizable by addition in the presence of said catalyst, admixing from about 55% to about 85% by weight of particulate high explosive having an average oxygen balance of not less than —47 with the monomer and catalyst, supporting the resulting mixture in form of a shell with a cavity therein for containing an initiating element, heating the supported mixture at a temperature not greater than about 100° C. until a solid polymerization product is obtained, and disposing an initiating element in said cavity.

8. A process of claim 7 wherein said ignition element is placed in said cavity prior to said heating.

References Cited in the file of this patent

UNITED STATES PATENTS

405,684	Smith et al.	June 18, 1889
1,700,085	Scott	Jan. 22, 1929
2,001,212	Olsen et al.	May 14, 1935
2,067,213	Snelling	Jan. 12, 1937
2,404,688	Bruson	July 23, 1946
2,513,391	Zenftman	July 4, 1950
2,539,824	Garber	Jan. 30, 1951

(Other references on following page)

OTHER REFERENCES

Bebie-Manual of Explosives, Military Pyrotechnics and Chemical Warfare Agents, The MacMillan Co., New York (1943), pp. 54, 91, 97, 114.

Fundamental Principles of Polymerization, by G. F. D'Alelio, John Wiley & Sons, New York, 1952, pp. 5–18, 30, 52.

The Chemistry of High Polymers, by C. E. H. Bawn, Interscience Publishers Inc., New York, 1948, page 4.

Fundamentals of Plastics, by H. M. Richardson & J. W. Wilson, McGraw, Hill Book Co., New York, 1946, 1st edition, pp. 16–23, 77–82.

Pages 78, 79 of Bebie already of record is added to the record.

High Molecular Weight Organic Compounds, by R. E. Burk and O. Grummitt, copyright in 1949, by Interscience Publishers, Inc., pages 227 and 228.