WATER-DESENSITIZED BLASTING CAPS

Richard Dow, Bloomingdale, and Carl R. Hutter, Pompton Lakes, N.J., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

Filed Aug. 3, 1966, Ser. No. 569,741
3 Claims. (Cl. 102--28)

ABSTRACT OF THE DISCLOSURE

A blasting cap for underwater use adapted to be desensitized after a predetermined period of exposure to water by the ingress of water through at least one hole in the casing after dissolution of a water-soluble granular material.

Disclosure

For activities in which the detonation of explosive charges below the surface of the water is desired, such as in seismic exploration, underwater signaling, echo-ranging for detection purposes, and the destruction of undersea craft, there is needed a reliable and accurate blasting cap which can be actuated within a predetermined period after being submerged in water, e.g., about 2--60 minutes, and desensitized after a more prolonged exposure to water; the cap thus being incapable of inadvertent actuation if washed ashore.

Previously a blasting cap, used in coal mining, has been proposed comprising a casing with an opening or openings in its side walls (openings being adjacent to the primer charge), a water-soluble capsule within the casing and adapted to close the openings in the outer casing, and an explosive charge within the capsule. When such a cap is unactuated and remains in the broken-down coal, the washing water directed into the coal formation dissolves the capsule sufficiently to open the openings or slots. Thus, the primer charge is washed out of the casing and away through the openings which are opposite or adjacent to the explosive charge or charges. These caps, which are proposed in U.S. 1,901,469 (to Piccard), are inapplicable to underwater use, since the rapid washing away of the explosive charge would preclude their actuation after submergence. Blasting caps for use in oil wells have been proposed which are rendered inoperative by the action of fluid mud or other viscous fluid entering the cap through at least two ports in the shell, one adjacent to the ignition composition to the priming charge to expel air as cited in U.S. 2,739,535 (to Rolland, Shoener and Young). A similar device is found in U.S. 2,759,417 (to O'Neil) which describes an EBC for use in jet perforator assemblies which has vent holes in the shell of the cap between the igniter charge and the priming charge. The cap is rendered non-functioning when the space between these charges is filled with liquid. Also, U.S. 2,891,477 (to Swanson) proposes a fluid-desensitized initiator for use in a jet perforator which comprises a detonator and a receptor spaced from one another in a shell having entry ports for liquid in the portion of the shell adjacent to the space between the end of the detonator and the end of the receptor. When the space is filled with a liquid, actuation of the detonator will not initiate the receptor. Each of these types of caps involves desensitization immediately after contact of the cap with liquid (washing water or fluid mud). Thus these caps are similarly inapplicable to underwater use in that they are totally incapable of actuation in an aqueous medium. Further, although these devices are rendered inoperative by the action of a viscous fluid, they are reactivated shortly after removal from that fluid.

Accordingly, a need still exists for an initiator which can be actuated for a predetermined period after being submerged in water; however, after more prolonged exposure to water, e.g., about two to sixty minutes, desensitization occurs so that it cannot be actuated by extraneous electric energy (friction or static) or impact if unintentionally washed ashore.

This invention provides an improvement in initiators, and particularly blasting caps comprising a tubular shell at least one water-sensitive explosive charge contained therein, usually comprising a base and priming charge at least one of which is water sensitive; and an ignition means for said charge. The improvement of this invention comprises providing a hole in the bottom or output end of said shell and a body of water-soluble granular material between the water-sensitive explosive charge and the water-soluble granular material.

The ignition means as well as the explosive charges used in the initiators of this invention as well as the explosive charges described hereinafter used therein can be of the conventional type and can include both electric ignition assemblies and safety or detonating cord-actuated ignition assemblies of the types well known to those skilled in the art. However, this invention is particularly useful with instantaneous electric blasting caps used for seismic prospecting. Preferred ignition assemblies for caps of this type are described more completely in U.S. 2,957,997 which is incorporated herein by reference.

As indicated above, the shell has a hole in its bottom which allows water to seep into contact with a water-soluble composition. The hole preferably is formed at the bottom of the tubular shell but can in some embodiments of this invention extend into the lower portion of the lateral walls of the tubular shell. The minimum diameter of the hole is usually about 5 mils, since holes of smaller diameter usually do not permit sufficient inflow due to the surface tension of the water. Depending on the rate of dissolution desired, the hole can be increased in size to a point where the bottom of the shell is, for practical considerations, altogether eliminated.

An additional method of regulating the rate of water flow into the cap optionally can be provided by a dissolution-rate modifier or similar baffling between the base charge and the water-soluble compositions device to retard the flow of water through the water-soluble composition and to more closely regulate desensitization time. Suitable water-soluble compositions, which preferably are provided as a separate layer but can be mixed with the base charge, include sugars (i.e., saccharides) such as glucose, sucrose, dextrose, maltose, sugar derivatives such as levulinic acid; urea; water-soluble vinyl polymers such as polyvinyl alcohol and polyvinyl acetate; sodium carboxymethyl cellulose; and alkali or alkaline earth metals salts, e.g. barium perchlorate, Ba(ClO₄)₂, calcium perchlorate, Ca(ClO₄)₂; magnesium nitrate, Mg(NO₃)₂; sodium nitrate, NaNO₃; or any similar substances which dissolve up to 100% after a predetermined time in water, e.g., about 2--60 minutes. Granulated sugars of 200 mesh to 30 mesh are preferred because of their low cost, good handling and loading characteristics, and compatibility with most explosive charges. The water-soluble granular materials can be used alone or in combination with each other and also can be combined with water-insoluble materials which further act as a dissolution-rate modifiers or baffles, e.g., a microcrystalline cellulose, nitrocellulose, or any fibrinous material such as cotton, polyester fiber, acetate fiber or rayon fiber. Water will take longer to flow through the dissolution-rate modifier and act on the water-soluble granular material than if only the water-soluble material were present. Therefore, the predetermined time, usually
about 2–60 minutes, of desensitization can be modified by means of the dissolution-rate modifier. The watersoluble material, upon insertion into the casing, normally is compressed with a pin pressure of 50 to 200 p.s.i. of compression.

After the water-soluble composition is dissolved, the charge is in contact with water. Water seeps through the base charge, e.g. by capillary action, and contacts the primer charge which then absorbs moisture. When sufficient moisture is absorbed this water-sensitive charge becomes inactivated. When the charge used is lead azide, 1 to 2 wt. percent of water is sufficient for deactivation. When the cap is initiated (acted upon by an ignition stimulus, e.g. electric energy, to the bridgewire), the ignition charge will function normally up to the priming charge, which, because it is wet, will not actuate and not function to actuate the base charge.

In addition to the water-soluble granular material, in a preferred form of this invention, a barrier, preferably a plastic barrier and especially of polyethylene can be inserted as a baffle between the base charge and the water-soluble composition in order to retard the flow of water, thus producing the same or similar results as the dissolution rate modifier. This barrier is supplied with one or more grooves or holes, e.g. 5 mils in diameter or greater, through which water can flow into the base charge. While regulating the inward flow of water, this barrier similarly helps retard the drying and consequent re-activation of the cap after the initial desensitization.

In order to describe the water-desensitized initiators of this invention in greater detail, reference now is made to the accompanying drawing which is a vertical cross-sectional view of an electric blasting cap of this invention. However, other types of initiators, e.g. safety fuse or LEDC-actuated initiators, may be desensitized by this method.

Referring now to the figure in greater detail, 4 represents a metal shell having a hole 13 at its base; adjacent to and covering the hole is the water-soluble granular material 12. A polyethylene cup 11 (optional) separates the water-soluble granular material 12 from the base charge 10 of a detonating explosive. The two lateral grooves 14 in the polyethylene cup 11 enable water to flow through into contact with the base charge which transmits water, e.g. by capillary action, to the primer charge 9 adjacent to the base charge 10. The primer charge 9 is usually pressed into the base charge, is more readily ignitable than the base charge 10. Above the primer charge 9 is an ignition assembly comprising an ignition cup 8, an ignition charge 5, and a cover charge 7 which completely covers the ignition load 5. Embedded in the ignition charge are the lead wires 1 (electrical conductors) which form, with the bridgewire 6, an electrical ignition means. The lead wires 1 are sheathed in insulation 2 and are positioned with the rubber sealing plug 2A which is held in place in the shell by means of crimps 3 in the shell 4.

The operation of the initiator of the invention is identical to that of conventional instantaneous initiators, e.g. the priming charge is actuated by the deflagrating ignition charge (which is ignited by a hot bridgewire or the initiation impulse from a safety or detonating fuse) and initiates the base charge. However, if the cap is not actuated with a predetermined period of time, e.g. about 2–60 minutes, after the explosive charge is immersed in water at a predetermined depth, e.g. about 5–10 p.s.i. (10–25 ft.), the primer charge will be desensitized due to its absorption of water. The water-soluble granular material 12 dissolves at a predetermined rate when and as water enters the hole 13. After the watersoluble composition 12 dissolves, the base charge 10 comes into contact with water which in turn enters and desensitizes the priming composition. The base charge could possibly flow out the hole of the cap; however this would take considerable time, and would have no detrimental effect on desensitization. Generally with lead azide primers, the absorption by the primer charge of at least 1–2% water (by weight of the primer charge) is sufficient to cause its desensitization. Detonation stops at the junction between the primer and ignition charges since the ignition charge 5 will burn out without actuating the primer charge.

From the foregoing description it can be seen that the invention provides a dependable blasting cap which becomes desensitized at a regulatable interval after immersion in water.

The hole formed in the base of the shell preferably is greater than about 20 mils in diameter and can be as large as the inner diameter of the shell but usually is 50–100 mils in diameter. It is preferably approximately in the center of the bottom end of the shell, and can be produced by pressing with a heading pin, drilling, or punching. Naturally the size of this hole will regulate the rate at which water enters the shell. The layer of water-soluble composition typically consists of 0.5–5.0, and preferably 1.0–3.0 grains of sugar or correspondingly more of the other water-soluble granular materials, e.g. urea, polyvinyl alcohol, carboxymethyl cellulose, with a thickness depending on the density and desired dissolution rate of the particular material.

If sugar is used the dissolution rate is generally about 8 grains per hour. This rate of solubility is based on a number of things including the amount and the speed at which the water enters the hole of the cap, the compactness of the layer of water-soluble composition with the base charge, the density of the water-soluble composition, and the effects of the dissolution-rate modifier on the water-soluble composition. In general the rate at which water enters the shell will increase with increasing the size of the hole in the shell and will decrease when the water-soluble granular material is firmly packed and/or a dissolution-rate modifier is present.

The polyethylene cup is typically 1/4 inch in length and after insertion into the shell on top of the water-soluble composition is typically pressed at 50–200 p.s.i., with a heading pin. The shell can be constructed of a metal, e.g. thin gauge copper, commercial bronze, other copper alloys when the primer charge is any explosive charge other than lead azide (hazard—when copper is exposed to lead azide in the presence of moisture, hazardous copper azide is formed). Preferred shell materials for use with lead azide are aluminum or polymeric materials having comparable structural strength and rigidity. As may be seen the thickness of the shell should be sufficient to retain the charges. The exact length of the shell will depend upon the size of the charges, and the nature of the ignition assembly, and the length of the delay element and/or dissolution-rate modifier, if any, to be incorporated in the initiator, but will usually vary between about 1.0 and 5.5 inches. Ordinarily standard shell diameters are used, e.g. shells having an outer diameter of about 0.281–0.288 inch and an inner diameter of about 0.260–0.259 inch.

The particular compositions used for the various charges are not of main importance to the present invention as long as at least one explosive charge, and preferably the primer charge is desensitized on contact with moisture. Accordingly, for the base charge, any of the conventional base charges can be used, e.g. pentaerythritol tetranitrate (PETN), lead azide, cyclohexylmethylene-nitramine (RDX), nitromannite, trinitrotoluene (TNT), or cyclohexylmethylene-trinitramine (HMX). As the primer charge, heat-sensitive detonating compositions are used. Preferred water-sensitive explosives include inorganic azides, such as lead azide, nitrammite, nitrophens such as diazidinitrophenol, or combinations thereof such as complex salts of lead nitrate and lead di-nitro - o - cresylate in combination with lead azide can be used. Typical ignition compositions used in the preferred electric initiator embodiment of this invention include the complex salt of lead nitrate with a lead salt of a nitrophens, mercury fulminate, lead styphnate, tetryl-
lead styphnate compositions, diazodinitrophenol, nitromannite compositions, etc. It should be noted here that the previously mentioned compositions are insoluble or almost insoluble in water and are nonhygroscopic or have a low hygroscopic percentage.

In order to desensitize one or more of the explosive charges, killing agents which react with the explosive when it is wet can be added thereto. For example, for lead azide such agents include ceric ammonium nitrate, ceric ammonium sulfate, and a mixture of sodium nitrite and acetic acid or any mineral acid, e.g. nitric or sulfuric acid.

The following example illustrates the performance of this invention.

**Example**

A number of initiators are assembled as shown in FIGURE 1.

These caps are designed to be completely desensitized by exposure to water after 60 minutes but to function normally for up to fifteen minutes after being in contact with water. In the interval of 15 to 60 minutes' exposure partial desensitization is effected. The shells are coined bottom aluminum with an outer diameter of 0.281 inch and an inner diameter of 0.260 inch. A hole 0.187 inch in diameter is punched approximately in the center of the bottom of the shell. Into the shells are loaded 2.0±0.1 gr. of "Jack Frost" or quick-dissolving sugar, of approximately 200 mesh serving as the water-soluble composition, and this composition is pressed with a polyethylene cup at approximately 200 p.s.i., the cup remaining as a barrier between the granular water-soluble composition and the base charge. Then 5±0.3 grains of 99.5/0.5 PETN or 90/10 PETN/sugar is used as the base charge. The priming charge consists of 2.2 grains of 85/15 dextrinated lead azide/coarse lead salt pressed into the shell with a second plastic (polyethylene) cup which is inserted between the primary charge and 2.0 grains of unpressed lead styphnate serving as the ignition composition. The cover charge consists of 1.1 grains of lead salt. Plastic insulated tinned 20-gage duplex copper lead wires and 0.210 inch crimps are used. As shown in the table, these caps are subjected to tests in air at 0 p.s.i. or in water at 5–10 p.s.i. The tests in water are placed in 10–25 feet (5–10 p.s.i.) of salt water which is contained in a steel pipe standing vertically in a 10-foot well filled in most cases with natural sea water (simulating the ocean). For some tests artificial agitation is produced by the movement of strings in the pipe to give a wave effect to the water in the pipe. However, the absence or presence of agitation has little influence on the effect of desensitization. The caps which are placed in water at 5 p.s.i. (about 11 feet depth) for less than 2 minutes detonate when an ignition stimulus is applied; therefore desensitization does not occur and the caps function normally. Normal functioning involves initiation of the cap to induce action up to and including the base charge. After 60 minutes or more at 5–10 p.s.i. desensitization takes place and all caps fail. (As used herein, failure of a cap signifies that the cap functions up to and including the ignition composition but the primer charge does not function, thus desensitization occurred.) The primer charges are not able to be actuated since water entered the cap and seeped through the base charge, e.g. by capillary action and contacted the primer charge which then absorbed moisture and became inactivated. Since the primer charge is inactivated the ignition charge burned out. Other caps exposed to sea water for about 4 p.s.i. at 10 feet depth for 6 hours (time) were tested by drying them for 45–50 hours in 120° F. and then tested (actuated) in air at 0 p.s.i. These caps did not function, thus they were desensitized since the primer charge, having absorbed moisture, was not able to be actuated by the ignition charge.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Shot In</th>
<th>Pressure (p.s.i.)</th>
<th>Time of Exposure to Water (mils)</th>
<th>No. of Tests</th>
<th>Type of Detonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Salt water</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>2 detonations.</td>
</tr>
<tr>
<td>2</td>
<td>do.</td>
<td>5</td>
<td>15</td>
<td>5</td>
<td>2 detonations.</td>
</tr>
<tr>
<td>3</td>
<td>do.</td>
<td>5</td>
<td>1</td>
<td>3</td>
<td>2 failures.</td>
</tr>
<tr>
<td>4</td>
<td>do.</td>
<td>5</td>
<td>15</td>
<td>5</td>
<td>2 detonations.</td>
</tr>
<tr>
<td>5</td>
<td>do.</td>
<td>5</td>
<td>60</td>
<td>5</td>
<td>2 failures.</td>
</tr>
<tr>
<td>6</td>
<td>Air</td>
<td>10</td>
<td>60</td>
<td>3</td>
<td>2 failures.</td>
</tr>
<tr>
<td>7</td>
<td>Air</td>
<td>10</td>
<td>13</td>
<td>5</td>
<td>2 failures.</td>
</tr>
<tr>
<td>8</td>
<td>Air</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>2 failures.</td>
</tr>
<tr>
<td>9</td>
<td>Air</td>
<td>10</td>
<td>16</td>
<td>2</td>
<td>2 failures.</td>
</tr>
</tbody>
</table>

1 Previously, in 4 p.s.i. of water.

It can be concluded that at 5 p.s.i. or greater in water actuation definitely takes place up to 2 minutes, but within the predetermined time period usually of about 2–60 min. detonations and/or failures can occur with water desensitized caps. However, after still longer exposure (greater than the predetermined period of time) desensitization occurs and the caps are not capable of actuation, therefore eliminating the danger of inadvertent actuation should the caps be washed ashore.

The above example can be conducted with similar results by the substitution in place of the sugar, of one grain of "Elvanol" polyvinyl alcohol, or one grain of 75/25 mixture of urea and polyvinyl alcohol, at the same time increasing the size of the hole formed in the base from 77 to 100 mils.

We claim:

1. An initiator comprising a tubular shell, at least one water-sensitive explosive charge contained therein, and a means for the ignition of said explosive charge in said shell, the improvement comprising providing at least one hole in said tubular shell in the end opposite that having the ignition means, a body of water-soluble granular material between said hole and said water-sensitive explosive charge, and a barrier inserted between said water-soluble granular material and said water-sensitive explosive charge, said barrier having at least one aperture therein.

2. A blasting cap of claim 1, wherein said water-soluble granular material is sugar.

3. A blasting cap of claim 1, in which said barrier is a polyethylene cup having two lateral grooves formed therein with a diameter of 6 mils.

References Cited

UNITED STATES PATENTS

2,362,192 11/1944 Delalande ———— 102–16
2,379,372 10/1966 Patterson ———— 102–28
2,322,066 5/1967 Griffith et al. ———— 102–24

BENJAMIN A. BORCHELT, Primary Examiner.
SAMUEL FEINBERG, Examiner.

V. R. PENDEGRASS, Assistant Examiner.