A process for the production of a thermal shock tube is used to form a product that is utilized as a transmission device for connecting and initiating explosive columns, or as a flame conductor. The device is usually complemented by a delay element or used as a delay unit. The thermal shock tube uses a pyrotechnic mixture with low sensitivity to ignition by shock or friction, with low toxicity, and which generates a spark with superior thermal performance. The process utilizes continuous and separated dosing of the individual non-active components, in conjunction with the formation of the plastic tube, making the process safer, and with a more accurate dosing. The product maintains the advantages of current art pyrotechnic shock tubes relative to the shock wave propagating tube, e.g. larger transmission sensibility and sensitivity, propagation even with cuts or holes in the tubes, and low risk transport classification. The product has the additional advantages of using low toxicity components, use of ordinary, low cost, low adhesiveness polymers, the generation of a spark that propagates through knots, closed kinks or tube obstructions, and resistance to failure due to attack of components by hot explosive emulsions.
PROCESS FOR THE PRODUCTION OF A THERMAL SHOCK TUBE, AND THE PRODUCT THEREOF

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

The present invention relates generally to explosive signal transmission devices, and more particularly to a thermal shock tube and the method of manufacturing the shock tube.

[0002] 2. Description of the Prior Art

Since at least the 1970's, low energy signal fuses known commercially as "non-electric detonators" or "shock tubes", have been widely used for connecting and initiating explosive charges in the mining and quarrying industries. Such devices, marketed with brands like NONEL, EXEL, BRINEL, etc., came to be substituted for electric blasting caps ignited by metallic wiring, and represented a revolution in the market of detonation accessories, due to the ease of connection and application, and to the intrinsic safety against accidental ignition by induction of spurious electric current.

[0003] 3. Current processes and products that use high explosives as components (hereinafter referred to as "conventional shock tubes") are exemplified by the following:

[0004] 1) U.S. Pat. No. 3,590,739 is the original reference for a conventional shock tube. The reference describes a process of plastic extrusion forming a circular tube with an outer diameter varying from 2.0 to 6.0 mm and an inner diameter varying from 1.0 to 5.0 mm. A secondary explosive powder, such as HMX, RDX or PETN, is introduced into its inner periphery during formation of the tube. The resulting product is known as a non-electric shock tube, and is marketed with trade names such as NONEL and EXEL.

When initiated by a primary explosive blasting cap, a conventional shock tube generates a gaseous shock wave with a signal transmission speed ranging from 1,800 to 2,200 m/s. Further improvements include the addition of aluminum to increase specific energy and utilization of ionomeric polymers, like SURLYN, to increase adhesiveness of the powder.

[0005] 2) U.S. Pat. No. 4,328,753 describes a conventional shock tube with two layers: an inner layer made of a polymer which provides adhesiveness to the explosive powder mixture, and an outer layer made of a polymer which provides mechanical strength. SURLYN is most suitable for the inner polymer layer, and polypropylene, polyamide, or polybutene is used for the outer layer. This product was an improvement over the original NONEL tube, as SURLYN alone is expensive and has a low resistance to external damage.

[0006] 3) European patent EP 027 219, and the related U.S. Pat. Nos. 5,317,974 and 5,509,355 describe a single-layer shock tube, and its method of manufacture, in which the polymer is Linear Low Density Polyethylene (LLDPE) with minor quantities of an adhesive promoter. The tube is made by extrusion of an initial tube with outer and inner diameters greater than that of the final tube. Then the tube is stretched in order to orient the LLDPE molecules, making a final tube with greater tensile strength. All claims are for a minor amount of an adhesion promoter in the polymer formulation, as it is well recognized in the art that powders have a low adherence to LLDPE. However, the best conventional shock tubes continue to be made in two layers, and the inner layer continues to be SURLYN, as even a low dislodgement of poorly adhered explosive powder may lead to failures in signal propagation due to discontinuities in the powder layer or by concentration of loose powder in the lower parts of the tube during field application.

[0007] 4) U.S. Pat. No. 5,166,470, describes a single-layer tube of LLDPE similar to that of EP 027 219, but with an additional thin layer of a hydrophilic polymer, like Polyvinyl Alcohol (PVA), is deposited by passing the plastic tube through a solution of polymer in a liquid, e.g. water, and drying the solvent. The aim is to make the tube less permeable to the hydrocarbons present in an emulsion explosive. Hot diesel fuel is particularly aggressive to LLDPE, and prolonged contact of the tube with hot, diesel fuel-based emulsions causes failure in signal propagation. The PVA protective skin is fragile and does not adhere well to the LLDPE, and so a pretreatment with a cleaner (like chromic acid), with hot air or with an adhesion promoter (like Vinamul EVA copolymer) is necessary.

[0008] A further development in low energy transmission fuses was the invention of tubes that make use of pyrotechnic mixtures inside the tube, as substitutes for high-explosive-containing powders. Currently, some of the processes and products with pyrotechnic mixtures, hereinafter referred to as "pyrotechnic shock tubes", are the following:

[0009] 1) Brazilian patent PI 8104552, from the applicant of the present patent, is the original reference for the pyrotechnic shock tube. It describes a process of plastic extrusion forming a circular tube with an outer diameter ranging from 2.0 to 6.0 mm, and an inner diameter ranging from 1.0 to 5.0 mm. A powder of pyrotechnic mixture of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>+Al or Mg, Fe<sub>3</sub>O<sub>4</sub>+Al or Mg, or Sb<sub>2</sub>O<sub>3</sub>+Al or Mg, is introduced in the inner periphery of the tube during formation of the tube. The resulting product is designated as a pyrotechnic shock wave tube, and marketed with the trade name BRINEL. When initiated by a primary explosive detonator, such a tube generates an aluminothermic reaction without gas releases, and develops a plasma for energy transmission.

[0010] 2) U.S. Pat. No. 4,757,764 describes a non-electric system for controlling an initiation signal in blasting operations using a plastic tube with pyrotechnic delay mixtures adhered to its interior. This device uses slow speed reactions, with much slower speeds than those of conventional shock tubes and detonating cords, with the object being to use predetermined lengths of tube to obtain a delay time in the milliseconds range, the tube being substituted for a conventional delay element. The blasting caps connected to the plastic tube are necessarily instantaneous, without delay elements in the cap. There was therefore no attempt by the inventor to optimize the thermal action of a spark, nor to eliminate toxic components, nor to guarantee the crossing through restrictions in the tube. Similarly, there was no effort to reduce the sensitivity of the mixture to friction and mechanical shock, or to address the adhesiveness of the mixture to the tube. There was also no consideration of the resistance to attack by hot hydrocarbons from the emulsion explosive. It is evident, by the patent's descriptive report, and from all of the examples, that its use as a delay element...
is limited to the range of tens of milliseconds, which is not adequate for most of the delays required in field practice.

[0013] Signal transmission tubes are usually complemented with the insertion of a delay blasting cap in the tip of the tube. The blasting cap is made of a metal cap containing two layers of explosive powder pressed inside. The bottom layer is a secondary high explosive, and the upper layer is a primary, flame-sensitive explosive. The cap further includes a delay element consisting of a metallic cylinder containing in its interior a compacted column of powdery pyrotechnic delay mixture and, frequently, an additional column of pyrotechnic mixture sensitive to the heat generated by the tube's shock wave.

[0014] The process for the manufacture of a conventional shock tube, as well as the resulting product, presents the following disadvantages:

[0015] a) The production of the tube loaded with explosives (RDX, HMX or PETN) is toxic and dangerous) offers risks both of accidental explosions and in the handling toxic products, requiring special care and protection in the production line. The fact that molecular explosives are used impedes the dosing of non-active components during the extrusion of the tube.

[0016] b) In the conventional shock tube, the reaction products are basically hot gases which, when leaving the final extremity of the tube, expand with loss of heat, such heat loss inhibiting the ignition of the pyrotechnic delay mixture. Slower delay powders are particularly insensitive to the shock tube output. It is therefore necessary either to add an additional column of a sensitive pyrotechnic mixture to give continuity to the explosive train or to use pyrotechnic mixtures more sensitive to heat and with larger column length. As a consequence, the final product has greater production costs, and the processing and handling of the pyrotechnic mixture entails significant accidental ignition risks.

[0017] c) The adherence of crystalline explosives (RDX, HMX or PETN) in plastic tubes is low, demanding special manufacturing processes and the use of special, and expensive, polymers, usually ionomeric polymers such as SURLYN, in order to minimize the concentration of loose powder in portions of the tube and to assure uniformity of distribution. Lack of adherence of LLDPE is particularly noteworthy. It is significant that the best known commercial brands of shock tube continue to use a two layer tube, with SURLYN as the inner layer, in spite of the efforts to improve polymer adhesiveness by changes in polymer formulation.

[0018] d) Conventional shock tube loading lacks sufficient critical mass and critical diameter to properly propagate a shock wave by classical detonation theory. The finding of the late Dr. Persson, inventor of the original shock tube, was that the shock wave is continuously sustained by dust explosion of the explosive powder dislodged by deformation of the plastic duct caused by the shock wave behind the reactive front. Due to this feature, a conventional shock tube fails if there is a cut or a close restriction in the inner duct, dispersing the shock wave. In field practice, if unexpected cuts, stretching, knots, holes, or closed kinks unexpectedly appear in the tube, the tube can fail to propagate.

[0019] e) Conventional shock tubes are sensitive to the effect designated in the industry as “snap, slap, and shoot”. An unexpected ignition can occur if the tube is stretched causing rupture, in particular conditions of mechanical energy release, as recognized in an article presented in the 28th Annual conference of the ISEE, Las Vegas, 2002, and in all catalogs and technical bulletins of conventional shock tubes.

[0020] f) Conventional shock tubes are classified for transport purposes as an explosive in many countries, which results in additional costs and difficulties for transportation, especially after the increase in dangerous products regulations resulting from the fight against terrorism.

[0021] g) Conventional shock tubes can fail to propagate after prolonged underwater exposure above 2 bar pressure, as is often found in field practice, due to the hydrophilic characteristics of the ionomeric resins like SURLYN.

[0022] h) Tubes manufactured with SURLYN alone have a low tensile strength, and a low resistance to abrasion, kinks, knots, etc., demanding co-extusion of an additional outer layer of polyethylene. This improved process still includes the use of expensive SURLYN.

[0023] i) Conventional explosive powders lack sufficient activation energy to propagate in case of contamination of the tube interior by hot hydrocarbons (most likely diesel fuel) from explosive emulsions. Polymers, including LLDPE, are quite susceptible to aggression. Minor quantities of adherence-improving additives, typically EVA copolymers, are even more subject to attack by volatile fractions of diesel fuel. An additional skin of hydrophilic polymer like PVA is needed, but abrasion resistance of the skin, particularly in the rough environmental conditions found in field practice, is remarkably bad, causing removal of the skin and failures of the tube.

[0024] j) According to the specifications published by the manufacturers, conventional shock tube speeds of deflagration range from 1,800 to 2,200 m/s, or within 10% of a mean speed of 2,000 m/s. This relatively broad range interferes with the accuracy of the delay element timing. U.S. Pat. Nos. 5,173,569, 5,435,248, 5,942,718, and Brazilian patent PI 9502995, from the author, all use a shock tube as the initiator of an electronic delay blasting cap. Such caps are characterized by a highly accurate electronic delay element. However, the timing error of a certain length of tube is added to the intrinsic timing error of the electronic circuit. In a typical tube length of 21 m, as used in open pit mining, the error would be within +/-1 ms, while the intrinsic error of the electronic circuits is typically within +/-0.1 ms.

[0025] k) Conventional shock tube deflagration generates substantially gaseous reaction products, sustaining a shock wave that quickly disperses most of the released thermal energy, through the expansion of the gases as they leave the tip of the tube. For this reason, a conventional shock tube output is unable to ignite low flame-sensitive delay mixtures, demanding an additional, highly flame-sensitive, igniter element for ignition of the slower delay elements. Highly flame-sensitive mixtures are usually also highly sensitive to mechanical shock, friction and electrostatic discharge, increasing the risks of accidental detonation. The additional element also increases the manufacturing costs.

[0026] A pyrotechnic shock tube, as disclosed in Brazilian patent PI 8104552, from the applicant of the present patent, has the following disadvantages:
A) Pyrotechnic mixtures use toxic components (K₂Cr₂O₇, Sb₂O₃, Sb₂O₅) and flammable solvents, demanding recycling of the solvents, and creating handling issues and requiring appropriate waste disposal.

B) The process of extrusion of the plastic tube includes the dosing of a previously prepared sensitive pyrotechnic mixture during the formation of the plastic tube, with safety risks in handling and processing.

C) Like a conventional shock tube, a pyrotechnic shock tube does not resist aggression from the hydrocarbons present in emulsion explosives, and prolonged exposure leads to failures in propagation.

D) Mixtures of O₂+Al or Mg were not shown to be feasible in practice, due to the loss of gases in the production and use of the product.

E) Mixtures of Fe₂O₃+Al or Mg were also not shown to be feasible in practice, due to the low sensitivity of these pyrotechnic mixture to the ignition stimulus of bursting caps and a high rate of propagation failures. The fundamental cause proved to be the components high Tammann temperature.

F) Giving the limitations presented by shortcomings D and E, the only remaining options were highly toxic, highly friction and shock sensitive mixtures of K₂Cr₂O₇, Sb₂O₃, and Sb₂O₅ with Al or Mg.

G) The reaction products formed in the aluminothermy reactions, Al₂O₃, K₂O, Sb, antimony oxides, Cr₂O₃, necessarily solidified by the claimed limitations, have low thermal conductivity, which inhibits the ignition of slower, low sensitive delay elements.

H) Like conventional shock tubes, the powdered pyrotechnic mixture also presents a low adherence to the tube polymer, particularly in LLDPE.

I) Pyrotechnic mixtures are not optimized to allow propagation through closed knots, cuts or kinks.

The system for control of an initiation signal in blasting operations disclosed in U.S. Pat. No. 4,757,764 presents the following disadvantages:

Aa) As with the original pyrotechnic shock tube, the process also includes the dosing of a previously prepared sensitive pyrotechnic mixture, during the formation of the plastic tube, with safety risks in handling and processing.

Bb) The system makes use of direct tube-to-tube connections for supplying a time delay exclusively through a predetermined length of tube, and is limited to fast delays, in the range of tens of milliseconds, while field blasting operations demand delay timing up to 10 s.

Cc) The powdered mixtures, containing no adherence additive, present a low adhesiveness to the tube polymer, requiring the use of expensive material, like SURLYN or silicone, as can be seen in all of the examples in the descriptive report.

Dd) As the inventor’s aim was a system of delay obtained through a tube with substantially reduced speed, eliminating the delay element, and directly igniting the highly sensitive primary explosive inside the blasting cap, there was no optimization of the thermal performance of a transmission signal. A low speed mixture lacks the energy to directly ignite slower, low sensitive delay mixtures, and to propagate through close kinks, knots or cuts.

SUMMARY OF THE INVENTION

The present invention is a thermal shock tube and the method of manufacturing the shock tube. The shock tube is used as a signal transmission device for connecting and initiating explosive columns, or as a flame conductor. The device is usually complemented by a delay element, or it can be used as a delay unit. The shock tube uses a pyrotechnic mixture with low sensitivity to ignition by shock or friction, with low toxicity, which generates a spark with superior thermal performance. The manufacturing process utilizes continuous and separated dosing of the individual non-active components, in conjunction with the formation of the plastic tube, making the process safer and yielding a more accurate dosing. The resultant product maintains the advantages of current art pyrotechnic shock tubes relative to the shock wave propagating tube, i.e., larger transmission sensitivity and sensitivity, propagation even with cuts or holes in the tubes, and low risk transport classification. The shock tube of the present invention gives the following additional advantages: use of low toxicity components, use of ordinary, low cost, low adhesiveness polymers, generation of a spark that propagates through knots, closed kinks or tube obstructions, and resistance to failure by attack of components of hot explosive emissions.

The focus of the present invention is to obtain desirable characteristics in the polymers that form the tube, but not to optimize the pyrotechnic mixtures formulation, in order to use ordinary, low cost polymers. The new approach is also multipurpose, i.e., to obtain the greatest possible number of desirable characteristics through the formulation of the pyrotechnic mixture. The process and product from this invention have the following advantages over the current art shock tubes:

The thermal shock tube employs an optimized pyrotechnic mixture with low toxicity.

The process allows the continuous dosing and mixture of two non-active components during the extrusion process, the components being essentially insensitive to friction and shock before mixture, thereby substantially reducing the probability of accidental initiation in handling, and, in case of ignition of the tube during production, minimizing the damages by the deflagration of a very small amount of mixture.

The process yields a safer pyrotechnic mixture, with smaller sensitivity to friction and mechanical shock, by covering the oxidizer components with a desensitizing additive.

The pyrotechnic mixture has an excellent adherence to the plastic tube, using low cost, common polymers, including LLDPE, and avoiding tube portions with lack or excess of charge.

The product maintains some advantages of the current pyrotechnic shock tube in relation to a conventional shock tube, e.g. a larger sensitivity and
sensitivity of propagation, propagation even with cuts or holes, and low risk classification for transport.

[0048] The spark of signal transmission is formed as much by gases as by melted metals, and so it crosses knots, closed kinks or obstructions in the tube, and presents an optimized heat transport by thermal conduction and convection, igniting less sensitive, slower delay columns directly.

[0049] The thermal shock tube resists environmental exposure to marine diesel fuel present in hot explosive emulsions, maintaining functionality even after 72 hours of exposure at high temperature (65 deg. C. for 24 h+40 deg. C. for 48 h in pure marine diesel).

[0050] The thermal shock tube has propagation speed accuracy within ±1.67% from the mean speed, i.e., an error of ±120 m/s in 1,200 m/s, adding to electronic delay detonators only ±0.3 ms of error in a 21 m long tube.

[0051] Objectives considered during development of the present invention included:

[0052] Elimination of poisonous components of the pyrotechnic mixture;
[0053] Improvement in the adherence of the mixture to the inner surface of the tube;
[0054] Desensitization of the mixture to shock and friction;
[0055] Decrease in handling risks of the pyrotechnic mixture;
[0056] Substitution of automated manufacturing processes for the pyrotechnic mixtures that were formerly labor-intensive, including grinding and recrystallization with dangerous solvents, and handling the pyrotechnic mixture by automated, risk-free, and environmentally-safe processes;
[0057] Generation of an optimized spark with excellent heat transfer by conduction and convection without dispersion of heat by gas expansion;
[0058] Production of a tube with functionality after exposure to hot, diesel fuel-based explosive emulsions up to 65 deg. C. for 3 days.

[0059] These and other objects and advantages of the present invention will become apparent to those skilled in the art in view of the description of the best presently known mode of carrying out the invention as described herein and as illustrated in the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0060] FIG. 1 shows a block diagram of the manufacturing process for the thermal shock tube of the present invention.

[0061] FIG. 2 shows the thermal shock tube spark as it leaves the tube tip.

[0062] FIG. 3 shows the basically gaseous products of a conventional shock tube when leaving the tube tip.

DETAILED DESCRIPTION OF THE INVENTION

[0063] One of the fundamental concepts for the understanding of the present invention was described by the Russian chemist Tamman. According to his theory, the vibrational energy needed to start an oxidation-reduction reaction among solid substances is largely available at the temperature equivalent to half the melting point of the substance, in the absolute scale (K). This temperature of Tamman explains why certain components make pyrotechnic mixtures quite sensitive to heat to flame and mechanical shock, while other ones are quite difficult to start an propagate. For example, mixtures of powdered aluminum, whose temperature of Tamman is 193 deg. C. and ferrous-ferric oxide, Fe2O3, whose temperature of Tamman is 632 deg. C. are particularly difficult to start and propagate, while mixtures of powdered aluminum and potassium chlorate, whose temperature of Tamman is only 47.5 deg. C., is especially dangerous. One of the invention objectives is to obtain enough activation energy to ensure the initiation and propagation of the pyrotechnic reaction even with contamination of the interior of the tube by hydrocarbon fuel coming from the explosive emulsion, such contamination decreasing the enthalpy pyrotechnic reaction. Examples of low-Tamman temperature substances suitable for the pyrotechnic mixture are potassium perchlorate, potassium chlorate, antimony trisulfide, sulfur, potassium nitrate, ammonium perchlorate, sodium chlorate, or any other substance whose temperature of Tamman is adapted to this purpose.

[0064] A pyrotechnic reaction that generates products with high thermal conductivity and thermal convection coefficient will allow better propagation continuity, and will ignite delay elements with greater thermal efficiency, allowing the use of smaller, slower delay columns without additional ignition elements. As relevant oxidation-reduction reactions, we have:

[0065] 8 Al + 3 Fe2O3 → 4 Al2O3 (solid) + 9 Fe (liquid) or,
[0066] 2 Al2O3 + 3 Fe → 2 Al2O3 (solid) + 2 Fe (liquid)

[0067] where the melted metallic iron supplies an excellent heat transfer, as much by thermal conduction as by convection.

[0068] The generation of solid or liquid products will not allow propagation through knots, kinks, restrictions, etc. It is necessary that enough gas volume be generated to allow the elastic expansion of the polymer around the fold or restriction, forcing the propagation of the spark. However, the gas volume cannot be excessive, or there will be dispersal of the solid and liquid products of the spark in the tip of the tube, combined with the gaseous expansion, that will provoke the loss of the thermal energy necessary for ignition of the delay element. Examples of components found to be appropriate for gas generation are antimony trisulfide, potassium perchlorate, potassium nitrate, sodium nitrate, ammonium perchlorate, sodium perchlorate, etc.

[0069] Certain products have lubricating properties and superficial adherence properties, which reduce the effects of
friction and mechanical shock of the mixture, and provide adhesiveness even to difficult polymers like pure LLDPE. Examples of such products are: talc (magnesium and aluminum hydroxide) and graphite.

[0070] Another unique feature of the process of the present invention is that the mixture of the oxidizers and additive is done separately from the fuels or reduction agents. The final active mixture is obtained in the plastic extruder, in an automated, continuous or semi-batch process, so that just a very small amount of pyrotechnic mixture is formed at any instant. This minimizes the hazard of an accidental ignition of the tube during production.

[0071] In order to allow propagation through cuts or holes accidentally made in the tube during use, the spark is constituted as much by products of high heat transfer as by gaseous products so that the heat transfer allows continuity of the pyrotechnic signal transmission so as to provide the mechanical impulse for releasing the spark from the open portion of the tube.

[0072] The development of the optimized formulation for the thermal shock tube was accomplished by several practical tests. For these tests, formulations of powdered pyrotechnic mixtures were closed by spraying in the inner diameter of the tube with melted pure LLDPE in an extruder. The tube was cooled, and stretched to obtain a 3.1 mm outer diameter, 1.4 mm inner diameter flexible tube. Conventional SURLYN shock tubes as well as prior art pyrotechnic shock tubes were sampled and tested as a comparison.

[0073] The tests used are as follows:

[0074] 1) Speed of propagation test: A tube portion with a length of 5 m is placed between two optical sensors linked to a precision chronometer. When the tube is ignited, the spark passes the first sensor to trigger the chronometer. When the spark passes the second sensor, the timing is ended. The propagation speed is obtained by dividing 5 by the time measured in seconds.

[0075] 2) Kink propagation test: In 10 samples, the tube spark should propagate through 10 closed 180° folds spaced by the same distance. This smallest distance among the following—m, 50 cm, 30 cm, 20 cm, and 10 cm—in which all 10 samples propagate completely, without failure, is recorded as “minimum distance between kinks”.

[0076] 3) Tight knot propagation test: a 1 m long tube sample is single-knoted in its middle section, and the tube extremities are held by a hydraulically-driven traction device, with a loading cell attached to measure the tensile strength to which the knotted tube is submitted. The tube is ignited, and the maximum load in which five successive samples propagate through the knot is recorded. The higher the maximum load, the better the ability of the tube to propagate through tight knots which could accidentally be made in field use. This test was performed for single-layer shock tubes, as well as for double-layer (LLDPE and SURLYN) conventional shock tubes, for comparison.

[0077] 4) Low energy detonating cord initiation: 100 samples of 1 m long tubes are connected to a line of detonating cord with a core loading of 2 grams/m of PETN, through a “J” type connector, and the detonating cord is initiated. The number of tubes which fail to propagate is recorded as “percentage of failures in initiation by 2 grams/m detonating cord”.

[0078] 5) Mechanical Shock Sensitivity: A sample of the pyrotechnic mixture powder is submitted to a known weight falling hammer, free-falling from a known height. The energy that causes 5 successive samples to deflagrate is recorded. The energy is calculated by the formula E=mgxh where m is the mass of the weight in free fall, g is the local acceleration of gravity, and h is the minimum height for ignition.

[0079] 6) Slower delay sensitivity: A delay element of 8.3 seconds delay time, with a 24 mm long column of pressed delay powder, containing slow delay mixture, without any additional igniting mixture, is placed at the end of a PVC tube with a 6 mm outer diameter, with variable length, with the tip of a 1.0 m long thermal shock tube, aligned in the other extremity. When the thermal shock tube is ignited, the spark should cross the free space from the hose interior and start the delay element. The larger the length of the hose in which the elements always ignited, the better the thermal performance of the spark. The largest hose length for ignition in 5 successive samples is recording as “sensitivity of the slow delay element”.

[0080] 7) Tube-to-tube “air gap”: A 3 m long thermal shock tube is transversally cut and the tube halves are moved a measured distance apart, maintaining their alignment through an aluminum guide in “half-pipe” format. The largest distance that the spark can cross the gap between the tube portions and initiate the second portion in 5 successive samples, is recording as “all-fire air gap”.

[0081] 8) Initiation after exposure to the hot explosive emulsion: 30 samples of 12 m long thermal shock tube, with the ends sealed by a rubber plug and a crimped aluminum cap, as is usual in the industry, are dipped in 65° C. hot bulk explosive emulsion with marine diesel oil as fuel, and placed in a lab stove at 65° C. for 24 hours. After this period, the stove has its thermostat lowered to 40° C., and the samples stay in the emulsion for 48 more hours, totaling 72 hours of exposure. The tubes are ignited and the percentage of failed tubes is recorded as “failures after exposure to the hot emulsion”.

[0082] 9) Adherence of the mixture to the tube: 10 tube samples 5 m long are weighed in an analytical scale with an accuracy of 0.0001 g. The interiors of the tubes are flushed by compressed air with a flow rate of 0.3 Nm³/minute for 2 minutes, to remove the non-adhered powder. The tubes are weighed again and the weight is recorded. The interior of the tubes is washed with a flow of sodium hydroxide aqueous solution for dissolution of the aluminum and perchlorate, and iron oxide and talc, eliminating the adhered powder. The empty plastic tube is weighed. After determination of the tube’s inner diameter the surface area is calculated and the free powder load by area rate, the adhered powder load by area rate, and the percent rate of free powder mass by total powder mass are calculated.

[0083] The test results are consolidated and summarized in the following Table 1.
According to the test results in Table 1, the formulation Al/Fe$_2$O$_3$/KClO$_3$/Talc in the respective percentiles 40/27.5/31.5/1.0 is optimal for the shock tube of the present invention. A high content of aluminum fuel with 65% Al, with a corresponding lower speed of 750 m/s, means an insufficient spark performance in the propagation through kinks and knots, and a very low sensitivity of the slow delay element. On the other hand, a very low aluminum fuel content, as in the formulation 30/32.5/36.5/1.0, will generate a very high gaseous volume, dispersing the spark products at the tube tip, reducing the sensibility of the slow delay element and the "all-fire air gap". The results confirm the efficacy of the talc in improving the adherence of the mixture to the tube and in decreasing the mixture shock sensibility.

The optimized formulation for the thermal shock tube is:

- 32% to 60% powdered aluminum. Other powdered fuels or reduction agents able to generate a high temperature spark, such as magnesium, silicon, boron and zirconium, could also be used.
- 15% to 35% of powdered ferrous-ferric oxide (Fe$_2$O$_3$). Other substances that in oxidation-reduction reactions generate products with high thermal conduction and convection, such as ferric-oxide (Fe$_3$O$_4$), ferrous oxide (FeO), cobalt oxide, cupric oxide (CuO), and cuprous oxide (Cu$_2$O) can also be used.
20% to 40% potassium perchlorate (KClO₃). Other substances of low temperature of Tammann, which are able to lower the energy of activation of the pyrotechnic reaction and to generate enough gaseous volume to propagate through kinks, knots, or tube restrictions, such as potassium chlorate, potassium nitrate, ammonium perchlorate, sodium perchlorate, sulfur, and antimony trisulfide, can also be used.

0.5% to 3.0% talc. Other substances able to promote adherence and to reduce shock and friction sensibility, such as graphite, can also be used.

Referring now to FIG. 1, the process for the production of a thermal shock tube is as follows:

a) The oxidizers and the adherence promoter and desensitizing additive are thoroughly mixed, forming mixture I;

b) Mixture I is fed into a dosing silo, and the fuels are fed into another dosing silo;

c) The balanced proportions of mixture I and the fuels are continuously dosed through two parallel dosing thread type devices or through vibratory dosers or any other conventional weight or volume microdosing means. The microdosing means include electric motors with frequency controllers or any other conventional controller in a control loop with the plastic tube extruder, so that balanced doses are continuously reaching a roll homogenizer-mixer with a bottom screen, producing the final sensitive pyrotechnic mixture in small quantities, the bottom screen being connected to the extrusion ring of the plastic tube extruder;

d) As the pyrotechnic mixture is being prepared, a melted polymer is extruded through the extruder ring forming a plastic tube. While the plastic tube is being formed, the pyrotechnic mixture is introduced by gravity dosing into the plastic tube. This yields the desired product, the thermal shock tube.

Additional optional processing steps include tube cooling, stretching of the tube to obtain a desired tensile strength, thermal treatment of the tube, and other techniques known in the plastic processing art.

The final product, a thermal shock tube according to the present invention, has a conventional plastic tube, such as EVA, POLYETHYLENE, LLDPE or SURLYN, with an outer diameter ranging from 2.0 to 6.0 mm, and an inner diameter ranging from 1.0 to 5.0 mm. The tube includes 5 to 40 mg/m of pyrotechnic mixture adhered to its internal walls.

FIG. 2 shows the thermal shock tube spark as it leaves the tip of the tube during propagation. The drawing represents a high velocity photograph of the tube spark. FIG. 2 shows the high temperature solid and melted products (1), such products including highly thermal conductive and convective melted iron, and the gaseous products (2), which are responsible for the melted jet projection at the tube tip.

FIG. 3 shows, for comparison, the basically gaseous products of a conventional shock tube (prior art) as they leave the tip of the tube during propagation. This drawing also represents a high velocity photograph of the tube flame, and it can be seen that the basically gaseous products (1) are being dispersed by gas expansion at the tube’s end. These comparative drawings (derived from the high speed photographs) clarify why a conventional shock tube fails to propagate through irregularities in the tube and does not have the ability to ignite low sensitive delay columns.

The above disclosure is not intended as limiting. Those skilled in the art will recognize that numerous modifications and alterations may be made while retaining the teachings of the invention. Accordingly, the above disclosure should be construed as limited only by the restrictions of the appended claims.

I claim:
1. A shock tube comprising:
   an outer tube formed by extrusion, with an interior region containing a pyrotechnic mixture, said pyrotechnic mixture comprising an oxidizer, a reduction agent, a substance with a low temperature of Tammann, and an adherence promoter.
2. The shock tube of claim 1 wherein:
   said pyrotechnic mixture comprises 32-60% oxidizer, 15-35% reduction agent, 20-40% substance with a low temperature of Tammann, and 0.5-3.0% adherence promoter.
3. The shock tube of claim 1 wherein:
   said oxidizer is from the class of powdered ferrous oxide, ferric oxide, cobalt oxide, cuprous oxide, and cupric oxide.
4. The shock tube of claim 1 wherein:
   said adherence promoter is from the class of talc and graphite.
5. The shock tube of claim 1 wherein:
   said desensitizing agent is from the class of potassium perchlorate, potassium chlorate, ammonium perchlorate, sodium perchlorate, sulfur, and antimony trisulfide.
6. The shock tube of claim 2 wherein:
   said oxidizer is from the class of powdered ferrous oxide, ferric oxide, cobalt oxide, cuprous oxide, and cupric oxide.
7. The shock tube of claim 2 wherein:
   said adherence promoter is from the class of talc and graphite.
8. The shock tube of claim 2 wherein:
   said desensitizing agent is from the class of potassium perchlorate, potassium chlorate, ammonium perchlorate, sodium perchlorate, sulfur, and antimony trisulfide.

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