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(54) **PROCESS FOR PRODUCTION OF SPARK GENERATING TUBE, AND PRODUCT THEREOF**

VERFAHREN ZUR HERSTELLUNG EINES FUNKENERZEUGENDEN ROHRS UND PRODUKT DAVON

PROCEDE DE PRODUCTION D'UN TUBE GENERATEUR D'ETINCELLES ET PRODUIT OBTENU

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(56) References cited:
JP-A- 57 140 394
US-A- 5 101 729
US-A- 5 827 994
US-A- 4 522 665
US-A- 5 212 341

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Description

[0001] The present Patent refers to a process for production of a thermal shock tube and product thereof, applied as signal transmission device for connecting and initiating explosive columns, or as a flame conductor, usually complemented by a delay element or used as a delay unit, which uses a pyrotechnic mixture with low sensitivity to ignition by shock or friction, with low toxicity, which generates a spark with superior thermal performance, said process having the possibility of 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, and said product maintaining the advantages of the current pyrotechnic shock tube relative to the shock wave propagating tube: larger transmission sensibility and sensitivity, propagation even with cuts or holes in the tubes and low risk transport classification, and presents 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 emulsions.

[0002] Since the beginning of the decade of 1970, low energy signal fuses known commercially as "non-electric detonators" or "shock tubes", are broadly applied for connecting and initiating explosive charges in the mining and quarry sector. Such devices, marketed with brands like NONEL, EXEL, BRINEL, etc., came to substitute electric blasting caps ignited by metallic wiring, and represented a revolution in the market of detonation accessories, due to its easiness of connection and application, and to the intrinsic safety against accidental ignition by induction of spurious electric current.

[0003] Currently, the processes and products that use high explosives as components (hereinafter referred to as "conventional shock tube") are the following:

1) American patent US 3,590,739 is the original reference for conventional shock tube. It describes a process of plastic extrusion forming a circular tube with outer diameter varying from 2.0 to 6.0 mm and inner diameter varying from 1.0 to 5.0 mm, where it is continually introduced a secondary explosive powder, such as HMX, RDX or PETN, in its inner periphery, at the same time in which the tube is formed, the resulting product known as a non-electric shock tube, marketed with trade names such as NONEL and EXEL. When initiated by a primary explosive blasting cap, 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;

2) American patent US 4,328,753 describes a conventional shock tube in two layers, the inner layer made of a polymer which provides adhesiveness to the explosive powder mixture, and the outer layer made of a polymer which provides mechanical strength, being the most suitable inner polymer SURLYN and the outer polymer polypropene, polyamide or polybutene. This product was an improvement over the original NONEL tube, as SURLYN alone is expensive and has a low resistance to external damage;

3) European patent EP 027 219, and its continuations-in-part US 5,317,974 and US 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, and the tube is made by extrusion of a tube with outer and inner diameters greater than that of final tube, and then the tube is stretched in order to orientate 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. In spite of its claims, the best conventional shock tubes continue to be made in two layers, and the inner layer continue to be SURLYN, as even a low dislodgement of bad-adhered explosive powder leave to failures in signal propagation by discontinuities in powder layer or by concentration of loose powder in the lower parts of the tube during field application;

4) American patent US 5,166,470 describes a single-layer tube of LLDPE similar to that of EP 027 219, in which an additional thin layer of an hydrophilic polymer, like Polyvinyl Alcohol (PVA), is deposited by passing the plastic tube through a solution of polymer in, e.g. water, and drying the solvent. The aim is to make the tube less permeable to the hydrocarbons present in emulsion explosive.

[0004] 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. PVA protective skin is fragile and does not adhere 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.

[0005] A further development in the low energy transmission fuses was the invention of tubes that make use of pyrotechnic mixtures inside the tube, in substitution for high-explosive-containing powders. Currently, some of the processes and products with pyrotechnic mixtures, hereinafter referred as "pyrotechnic shock tube", are the following:

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 of outer diameter raging from 2.0 to 6.0 mm and inner diameter ranging from 1.0 to 5.0 mm, where it is continually introduced a powder of pyrotechnic mixture of $K_2Cr_2O_7$ + Al or Mg, Fe_2O_3 + Al or Mg, or Sb_2O_3+ Al or Mg, Sb_2O_5 + Al or Mg or O_2 + Al or Mg, in its inner periphery, at the same time in which the tube is formed, the resulting product being denominated pyrotechnic shock wave tube, marketed with trade name BRINEL. When initiated by a primary explosive detonator, such tube generates an aluminothermy reaction without gas releases, and develops a plasma for energy transmission;

2) American Patent US 4,757,764 describes a non-electric system for control of a initiation signal in blasting operations using a plastic tube with pyrotechnic delay mixtures adhered in its interior, particularly using low speed reactions, in much smaller speeds than that of the conventional shock tubes and detonating cords, with the aiming of using predetermined lengths of tube for obtaining a fast delay time in the milliseconds range, in substitution to the conventional delay element. The blasting caps connected to the plastic tube are necessarily instantaneous, without delay elements into the cap, and so there was no concern of the inventor in optimizing the thermal action of a spark, nor in eliminating toxic components, nor in guaranteeing the crossing through restrictions in the tube, nor in reducing the sensibility of the mixture to friction and mechanical shock, not even with the adhesiveness of the mixture to the tube, nor with the resistance to the attack by hot hydrocarbons from the emulsion explosive. It is evident, by the patent's descriptive report, and for all of the examples, that its use as a delay element is limited to the range of tens of milliseconds, not being adequate for most of the delays used in field practice.

[0006] There is a variety of other low energy fuses advanced in patents, or in commercial use.

[0007] Signal transmission tubes are usually complemented with the insertion of a delay blasting cap in its tip, such cap made of a metal cap containing two layers of explosive powder pressed inside, the bottom layer being a secondary high explosive, and the upper layer being a primary, flame-sensitive explosive, complemented by 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.

[0008] The process for manufacture of conventional shock tube, as well as the resulting product, presents the following disadvantage:

a) The production of the tube loaded with explosives (RDX, HMX or PETN are toxic and dangerous) offers risks both of accidental explosions as in handling toxic products, demanding special care and protection in the production line. The fact of using molecular explosives impedes the dosing of non-active components during the extrusion of the tube;

b) In the conventional shock tube, the reaction products are basically hot gases which, when leaving the final extremity of the tube, expand themselves 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 necessary either to add an additional column of 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 larger production costs, and the processing and handling of the pyrotechnic mixture offers larger accidental ignition risks;

c) The adherence of crystalline explosives (RDX, HMX or PETN) in plastic tubes is low, demanding special manufacturing processes and the use of special, expensive, polymers, usually ionomeric polymers as SURLYN, in order to minimize the concentration of loose powder in portions of the tube and to avoid portions without loading. Lack of adherence of LLDPE is particularly noteworthy. It is significant that the best known commercial brands 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;

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, conventional shock tube fails if there is a cut or a close restriction in the inner duct, dispersing the shock wave. In field practice, in case of unexpected cuts, stretching, knots, holes, or closed kinks, the tube could fail to propagate;

e) Conventional shock tube is sensitive to the effect called in the industry *"snap, slap, and shoot":* it could happen unexpected ignition 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. The article and technical bulletins of some commercial shock tubes are incorporated here as references.

f) Conventional shock tube is classified for transport purposes as an explosive in many countries, what results in additional costs and difficulties for transport, mainly after the increase in dangerous products regulations due to the fight against terrorism;

g) Conventional shock tube presents failure in propagation after prolonged underwater exposure above 2 bar pressure, often found in field practice, due to the hydrophilic characteristics of the ionomeric resins like SURLYN;

h) Tubes manufactured with SURLYN alone have a low tensile strength, and a low resistance to abrasion, kinks, knots, etc., demanding co-extrusion of an additional outer layer of polyethylene. Although, this process does not avoid the use of expensive SURLYN;

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, most likely EVA copolymers, are even more subject to attack by volatile fractions of Diesel oil. An additional skin of hydrophilic polymer like PVA is needed, but abrasion resistance of the skin, in the rough environmental conditions found in field practice, is remarkably bad, causing removal of the skin and failures. The author performed a series of tests of PVA-covered tubes, and the low adherence of the skin was proved;

j) According to the specifications published by the manufacturers, Conventional shock tube speed of deflagration ranges 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. American patents 5,173,569, 5,435,248, 5,942,718, and Brazilian patent PI9502995, from the author, all use shock tube as initiator of 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 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;

k) Conventional shock tube deflagration generates substantially gaseous reaction products, sustaining a shock wave that quickly disperses most of the released thermal energy, through expansion of the gases when leaving the tip of the tube. For this reason, 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 accidental risks. The additional element increases the manufacturing costs;

[0009] Pyrotechnic shock tube, as foreseen in the Brazilian patent PI 8104552, from the applicant of the present patent, has the following disadvantages:

A) Pyrotechnic mixtures use toxic components ($K_2Cr_2O_7$, Sb_2O_3, Sb_2O_5) and flammable solvents, demanding recycling of the solvents, handling cares, and appropriate waste disposal;

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

C) Like conventional shock tube, pyrotechnic shock tube doesn't resist to the aggression by the hydrocarbons present in emulsion explosives, and prolonged exposure leads to failures in propagation;

D) Mixtures of O_2 + Al or Mg, were not shown feasible in practice, due to the loss of gases in the production and use of the product;

E) Mixtures of Fe_2O_s + Al or Mg, were not shown feasible in practice, due to the low sensibility of these pyrotechnic mixture to the ignition stimulus of blasting caps and a high rate of propagation failures. The fundamental cause proved to be the components high Tammann temperature;

F) Giving the limitations presented in the items D and E, the only remaining options were highly toxic, highly friction and shock sensitive mixture of $K_2Cr_2O_7$, Sb_2O_3, and Sb_2O_5 with Al or Mg;

G) The reaction products formed in the aluminothermy reactions, Al_2O_3, K_2O, Sb, antimony oxides, Cr_2O_3, necessarily solids by the limitations in the patents claims, have low thermal conductivity, what inhibits the ignition of slower, low sensitive delay elements;

H) Like conventional shock tube, 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 to closed knots, cuts or kinks.

[0010] The system for control of a initiation signal in blasting operations foreseen in the American Patent US 4,757,764 presents the following disadvantages:

Aa) Like happens in the original pyrotechnic shock tube, the process also includes the dosing of previously prepared sensitive pyrotechnic mixture, during the formation of the plastic tube, with safety risks in handling and process;

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 in its formulation, present a low adhesiveness to the tube polymer, demanding the use of expensive material, like SURLYN or silicone, as can be seen in all of the examples in descriptive report;

Dd) As the author'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;

"PROCESS FOR PRODUCTION OF THERMAL SHOCK TUBE AND PRODUCT THEREOF", was developed to overcome the problems in the process of manufacture and in the performance of the current shock tubes. The approach is a new one.
The focus of research in previous art was mainly 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 Patent application have the following advantages over the current 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, this components been all most practically insensitive to friction and shock before its mixture, in such way substantially reducing the probability of accidental initiation in handling, and, even in case of ignition of the tube during production, causing minimum damages by the deflagration of a very small amount of mixture;
- The process obtains a safer pyrotechnic mixture more, with smaller sensibility to friction and mechanical shock, by covering the oxidizers components with a desensitizing additive;
- Its pyrotechnic mixture obtains an excellent adherence to the plastic tube, using the same additive, even in low cost, ordinary polymers, including LLDPE, avoiding tube portions with lack or excess of charge;
- The product maintains some advantages of the current pyrotechnic shock tube in relation to conventional shock tube: a larger sensibility and sensitivity of propagation, propagation to cuts or holes, and low risk classification for transport;
- The spark of signal transmission is formed so 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.
- The thermal shock tube resists to the environmental exposure to marine Diesel oil present in the hot explosive emulsions, maintaining functionality even after 72 hours of exposure at high temperature (65 °C for 24 h + 40 °C for 48 h in pure marine Diesel);

- Thermal shock tube has a propagation speed accuracy within +/-1,67% from the mean speed, i.e., an error of +/- 20 m/s in 1,200 m/s, adding to electronic delay detonators only +/- 0.3 ms of error in a 21 m long tube.

FIELD OF THE INVENTION

[0011] Invention is based on the knowledge the inventor possesses of the production and use of the pyrotechnic shock tube BRINEL, from the applicant, complemented by research for additional objectives:

- Substitution of poisonous components of the pyrotechnic mixture;
- Improvement in the adherence of the mixture to the inner surface of the tube;
- Desensitization of the mixture to shock and friction;
- Decrease in the handling risks of pyrotechnic mixture;
- Substitution of manufacturing processes for the pyrotechnic mixtures that used labor-intense working, including grinding and recrystallization with dangerous solvents, and handling of bulk, sensitive, pyrotechnical mixture by automated, risk-free, and environmentally-safe processes;
- Generation of a an optimized spark with excellent heat transfer by conduction and convection without dispersion of heat by gas expansion;
- Production of a tube with functionality after exposure to hot, Diesel oil-based explosive emulsions up to 65°C for 3 days.

[0012] One of the fundamental concepts for the understanding of the obtained inventive effects was described by the Russian chemist Tammann. 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 Tammann 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. As example, mixtures of powdered aluminum, whose temperature of Tammann is 193°C and ferrous-ferric oxide, Fe_3O_4, whose temperature of Tammann is 632°C are particularly difficult to start and propagate, while mixtures of powdered aluminum and potassium chlorate, whose temperature of Tammann is only 47,5°C, is especially dangerous. One of the invention bases is to obtain enough activation energy to warranty the initiation and propagation of the pyrotechnic reaction even with the contamination of the interior of the tube by hydrocarbon fuel coming from explosive emulsion, such contamination decreasing the enthalpy pyrotechnic reaction. As low-Tammann temperature substances adequate to take part of the pyrotechnic mixture can be mentioned potassium perchlorate, potassium chlorate, antimony trisulfide, sulfur, potassium nitrate, ammonium perchlorate, sodium chlorate, or any substance whose temperature of Tammann is adapted to this purpose. The invention is also based, without being limited to this, in the observation that a pyrotechnic reaction that generates products with high thermal conductivity and thermal convection coefficient, will allow a 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 interesting oxidation-reduction reactions, we have:

$$8\ Al + 3\ Fe_3O_4 \Rightarrow 4\ Al_2O_3\ \text{(solid)} + 9\ Fe\ \text{(liquid) or,}$$

$$2\ Al + Fe_2O_3 \Rightarrow Al_2O_3\ \text{(solid)} + 2\ Fe\ \text{(liquid)}$$

where the melted metallic iron supplies an excellent heat transfer, so much by thermal conduction as by convection. Another observation in which the invention is based is that the simgle generation of solid or liquid products will not allow the propagation through knots, kinks, restrictions, etc. it is necessary that enough gas volume would be generated to allow the elastic expansion of the polymer around the fold or restriction, forcing the crossing of the spark. However, this gas volume cannot be excessive, otherwise there will be the dispersal of the solid and liquid products of the spark in the tip of the tube, combined with the gaseous expansion, what will provoke the loss of the thermal energy necessary for ignition of the delay element. Examples of appropriate components for gas generation are antimony trisulfide, potassium perchlorate, potassium nitrate, sodium nitrate, ammonium perchlorate, sodium perchlorate, etc. Another knowledge taken into account as base for the invention is that certain products present lubricating properties and superficial adherence properties, what reduces the sensibility to the friction and mechanical shock of the mixture, and provides adhesiveness even to difficult polymers like pure LLDPE. Examples of such products are: talc (magnesium and aluminum hydrosilicate) and graphite. Another objective of the invention is to obtain an unpublished process in that the mixture of the oxidizers and additive is done in separate from the fuels or reduction agents, and that the final active mixture is obtained in the own 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, minimizing the risks and effects of an accidental ignition of the tube during the industrial production. Another aspect taken as base for the invention is that, to propagate through eventual cuts or holes accidentally done in the tube during field application, the spark should be constituted so much by products of high heat transfer, as by gaseous products, in a way to happen both the heat transfer to allow the continuity of the pyrotechnic signal transmission as to allow the mechanical impulse for releasing of the spark for the open portion of the tube.

[0013] 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 dosed by spraying in the inner diameter of melted pure LLDPE in a 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, obtained from a major manufacturer, as well as prior art pyrotechnic shock tubes from the applicant, were sampled and tested as a comparison. For better understanding of the examples the tests are described as follows:

1) Speed of propagation test: A tube portion with a measure length of 5 m is put among two optical sensors linked to a precision chronometer. When the tube was ignited, the light of the spark, when passing by the first sensor, starts the time counting, and, when passing by the second sensor interrupts the time counting. The propagation speed is obtained dividing 5 by the time counted in seconds;

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: 1 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";

3) Tight knot propagation test: a 1 m long tube sample is single-knotted in its middle section, and the tube extremities are hold 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 recording. The higher is the maximum load, the better is the ability of the tube in propagating through tight knots which could accidentally be made in field application. This test was performed for single-layer shock tubes, as well as for double-layer (LLDPE and SURLYN) conventional shock tube, for comparison;

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 line of detonating cord is initiated. The number of tubes which failed to propagate is recorded as "percentage of failures in initiation by 2 grams /m detonating cord";

5) Mechanical Shock Sensibility: A sample of the pyrotechnic mixture powder is submitted to a know weight falling hammer, free-failing from a certain height. The energy in that 5 successive samples deflagrate is calculated by the formula $E = m.g.h$, 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;

6) Slower delay sensibility: 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 layer of igniting mixture, is placed at the end of a PVC hose of 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 will be considered the thermal performance of the spark. The largest hose length for ignition in 5 successive samples is recording as "sensibility of the slow delay element";

7) Tube-to-tube "air gap": a 3 m long thermal shock tube is transversally cut at the middle length and their half tubes are moved away with a measured spacing, maintaining there alignment through an aluminum guide in "half-pipe" format. The largest distance in than the spark, when crossing the free gap among the tube portions, initiate the second portion in 5 successive samples, is recording as "all-fire air gap";

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

9) Adherence of the mixture to the tube: 10 tube samples 5 m long are weight in an analytical scale with and accuracy

of 0.0001 g. Afterwards, the interior of the tubes is flushed by compressed air with a flow rate of 0.3 Nm^3/minute for 2 minutes, to remove the non-adhered powder. The tube is 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 dragging of iron oxide and talc, eliminating the adhered powder. The empty plastic tube is weighed. After determination of the tube's inner diameter the superficial area is calculated and, by difference, the free powder load by area rate, the adhered powder load by area rate, and the percentile rate of free powder mass by total powder mass are calculate.

[0014] Tests results are consolidated and summarized in the Table 1.

[0015] According to the test results in Table 1, the formulation Al/$Fe_3O_4KClO_4$TalC in the respective percentiles 40/27.5/31.5/1.0 presented the best performance. 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 sensibility 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". It is proved also the effect of the talc in improving the adherence of the mixture to the tube and in decreasing the mixture shock sensibility. Based in the accomplished research and in the practical tests it can be concluded that the formulation according to the invention for the thermal shock tube is composed by:

- 32% to 60% of powdered aluminum. Another powdered fuels or reduction agents able to generate a high temperature spark, such as magnesium, silicon, boron and zirconium could be used;

- 15% to 35% of powdered ferrous-ferric oxide - Fe_3O_4. Another substances that in oxidation-reduction reaction generates products of high thermal conduction and convection, such as ferric-oxide - Fe_2O_3, ferrous oxide - FeO, cobalt oxide, cupric oxide - CuO and cuprous oxide - Cu_2O could be used;

- 20% to 40% of potassium perchlorate - $KClO_4$. Another substances of low temperature of Tammann, 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, sodium perchlorate, sulfur and antimony trisulfide;

- 0.5% to 3.0% of talc. Another substances able to promote adherence and to reduce shock and friction sensibility, such as graphite, could be used.

[0016] The components of the pyrotechnic mixture formulation can have combined characteristics, in other words, the same substance component can have more than a function as mentioned above at the same time.

[0017] The characteristics of the components of the formulation can be applied to conventional shock tubes, individually or combined, with the aim of optimizing them to obtain a better performance, a higher safety in production and a decrease in the environmental and occupational health risks.

[0018] The present patent can be better understood by the following figures:

FIGURE 1: shows the block diagram of the process for production of the thermal shock tube;

[0019] According to FIGURE 1, the process for production is according to claim 3

[0020] Additional steps of processing could include tube cooling, stretching of the tube to obtain tensile strength, thermal treatment of the tube, and other techniques conventional in the plastic processing area, without loss for the invention teachings.

[0021] The final product, thermal shock tube, uses conventional plastic tube, such as EVA, POLYETHYLENE, LLDPE or SURLYN, with outer diameter ranging from 2.0 to 6.0 mm and inner diameter ranging from 1.0 to 5.0 mm and containing 5 to 40 mg/m of pyrotechnic mixture adhered to its internal walls;

TABLE 1 - Practical Tests Results

Formulation	Speed of propagation	Minimum gap between kinks in kink propagation test	Tight knot propagation	Low energy detonating cord initiation	Shock Sensibility	Slower Delay Sensibility	all-fire air gap	Initiation after exposure to the hot explosive emulsion	Adherence of the mixture to the tube (% of free powder)
*Al 65% * Fe_3O_4 17% $KClO_4$ 17% Talc 1.0%*	*750 m/s*	*Failure at any distance*	*3 f-kg*	*8%*	*9.2 N*	*8 cm*	*80 mm*	*25%*	*5%*
Al 50 % Fe_3O_4 24.5% $KClO_4$ 29.5% Talc 1.0%	*1170 m/s*	*1 m*	*8 f-kg*	*Zero*	*9.2 N*	*16 cm*	*100 mm*	*zero*	*3. 8 %*
Al40% Fe_3O_4 27.5% $KClO_4$ 31.5% Talc 1.0%	*1260 m/s*	*30 cm*	*11 f-kg*	*Zero*	*9.2 N*	*22 cm*	*120 mm*	*zero*	*4.0 %*
*Al 30% * FO_3O_4 32.5% $KClO_4$ 36.5% Talc 1.0%*	*1290 m/s*	*30 cm*	*12 f-kg*	*Zero*	*9.2 N*	*5 cm*	*15 mm*	*15%*	*3.2%*
Al/$K_2Cr_2O_7$ Standard for the pior-art Pyrotechnic shock tube	*1000 m/s*	*Failure at any distance*	*3 f-kg*	*Zero*	*3.8 N*	*8 cm*	*100 mm*	*30%*	*18.3%*
Mixture HMX/ Al/ Standard for the convention al shock tube single layer	*2000 m/s*	*1 m*	*2 f-kg*	*zero*	*3.8 N*	*Fails to ignite, even at zero distance*	*10 mm*	*not performed*	*not performed*

(continued)

Formulation	**Speed of propagation**	**Minimum gap between kinks in kink propagation test**	**Tight knot propagation**	**Low energy detonating cord initiation**	**Shock Sensibility**	**Slower Delay Sensibility**	**all-fire air gap**	**Initiation after exposure to the hot explosive emulsion**	**Adherence of the mixture to the tube (% of free powder)**
Mixture HMX/ Al Standard for the convention al shock tube double layer *comparative examples	*2000 m/s*	*50cm*	*8 f-kg*	*zero*	*3.8 N*	*Fails to ignite, even at zero distance*	*10 mm*	*not performed*	*not performed*
* comparative examples									

Claims

1. A spark-generating tube, **characterized by** a pyrotechnic mixture adhered to an inner wall of a plastic tubing comprising the following solid powdered substances:

   a) between 32% to 60% of a powdered fuel or reduction substance that generates a high temperature spark selected from the group consisting of aluminium, magnesium, silicon, boron and zirconium;
   b) 15% to 35% of a substance which generates products having high thermal conduction and/or convection properties selected from the group consisting of ferrosoferric oxide - Fe_3O_4, ferric oxide - Fe_2O_3, ferrous oxide - FeO, cobalt oxide CoO, cupric oxide - CuO or cuprous oxide - Cu_2O;
   c) 20% to 40% of a substance lowering the activation energy of the pyrotechnic reaction and generating gaseous products having a volume large enough to propagate through kinks, knots, or tube restrictions selected from the group consisting of potassium perchlorate - $KClO_4$, potassium chlorate or potassium nitrate, ammonium perchlorate, sodium perchlorate, sulphur or antimony trisulfide;
   d) 0.5% to 3.0% of a substance promoting adherence and reducing the shock and friction sensibility of the pyrotechnic mixture selected from the group consisting of talc or graphite.

2. A tube according to claim 1 **characterized in that** the optimized formulation of the pyrotechnic mixture thereof comprises:

   a. 32% to 60% of powdered aluminium;
   b. 15% to 35% of powdered ferrous-ferric oxide - Fe_3O_4
   c. 20% to 40% of potassium perchlorate - $KClO_4$
   d. 0.5% to 3.0% of talc.

3. A process for the production of a spark-generating tube, according to claim 1, comprising the steps of :

   a) thoroughly mixing:

      a substance selected from the group a) as defined in claim 1 and
      a substance selected from the group b) as defined in claim 1 and
      a substance selected from the group c) as defined in claim 1

   b) feeding said mixture (I) in a first dosing silo and substances a) of claim 1 in a second dosing silo;
   c) continuously dosing balanced proportions of said mixture (I) and said substances a) of claim 1 through two parallel dosing thread type devices or through vibratory dosers or any other conventional weight or volume micro-dosing means, provided with electric motors with frequency controller or,any other conventional controller in control loop with a plastic tube extruder, said dosed balanced proportions continuously reaching a roll homogenizer-mixer having a bottom screen, thereby making the final sensitive pyrotechnical mixture, said bottom screen being connected to an extrusion ring of said plastic tube extruder;
   d) simultaneously with step c) extruding a melted conventional polymer through said extrusion ring thus forming a plastic tube, thereby at the same time dosing, by gravity, the final pyrotechnic mixture inside the plastic tube being formed, thus obtaining the spark-generating tube.

Patentansprüche

1. Funkenerzeugendes Rohr, **gekennzeichnet durch** eine pyrotechnische Mischung, weiche an einer Innenwand eines Kunststoffrohrs anhaftet, umfassend die folgenden festen pulvrigen Stoffe:

   a) zwischen 32% und 60% eines pulvrigen Brennstoffs oder eines Reduzierungsstoffes, der einen Hochtemperaturfunken erzeugt, ausgewählt aus der Gruppe bestehend aus Aluminium, Magnesium, Silizium, Bor und Zirkonium,
   b) 15% bis 35% eines Stoffes, der Produkte mit hoher Wärmegleitfähigkeit und/oder Konvektionseigenschaften erzeugt, ausgewählt aus der Gruppe bestehend aus Eisen(II, III)-oxid - Fe_3O_4, Eisen(III)-oxid - Fe_2O_3, Eisen (II)-oxid - FeO, Kobaltoxid CoO, Kupfer(II)-oxid - CuO oder Kupfer(I)-oxid - Cu_2O;
   c) 20% bis 40% eines Stoffes, der die Aktivierungsenergie der pyrotechnischen Reaktion erniedrigt und gasförmige Produkte erzeugte die ein Volumen aufweisen, das groß genug ist, um sich **durch** Knickstellen, Knoten

oder Rohrverengungen zu verbreiten, ausgewählt aus der Gruppe bestehend aus Kaliumperchlorat - $KClO_4$, Kaliumchlorat oder Kaliumnitrat, Amoniumperchlorat, Natriumperchlorat, Schwefel oder Antimontrisulfid;
d) 0,5% bis 3% eines Stoffes, der die Anhaftung fördert und die Schlag- und Reibungsempfindlichkeit der pyrotechnischen Mischung vermindert, ausgewählt aus der Gruppe bestehend aus Talk und Grafit.

2. Rohr gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die optimierte Rezeptur der pyrotechnischen Mischung davon umfasst:

a. 32% bis 60% pulvriges Aluminium;
b. 15% bis 35% pulvriges Eisen(II)-Eisen(III)-oxid - Fe_3O_4;
c. 20% bis 40% Kaliumperchlorat - $KClO_4$;
d. 0,5% bis 3 % Talk.

3. Verfahren zur Herstellung eines funkenerzeugenden Rohrs gemäß Anspruch 1, umfassend die Schritte:

a) gründliche Mischen eines Stoffes ausgewählt aus der in Anspruch 1 definierten Gruppe a) und eines Stoffes aus der in Anspruch 1 definierten Gruppe b) und eines Stoffes aus der in Anspruch 1 definierten Gruppe c), dadurch Ausbilden einer Mischung (I);
b) Einführen der Mischung (I) in ein erstes Dosierungssilo und der Stoffe a) aus Anspruch 1 in ein zweites Dosierungssilo;
c) kontinuierliches Dosieren abgestimmter Anteile der Mischung (I) und der Stoffe a) von Anspruch 1 durch zwei parallele gewindeartige Dosierungseinrichtungen oder durch Vibrationsdosierungseinrichtungen oder beliebige andere herkömmliche Gewichts- oder Volumenmikrodosierungsmittel, die mit elektrischen Motoren mit Frequenzregler oder beliebigen anderen herkömmlichen Reglern in einem Regelkreis mit einem Kunststoffrohrextruder versehen sind, wobei die dosierten abgestimmten Anteile kontinuierlich einen Walzenhomogenisierungsmixer erreichen, der einen unteren Filter aufweist, wodurch die endgültige empfindliche pyrotechnische Mischung hergestellt wird, wobei der untere Filter an einem Extrusionsring des Kunststoffrohrextruders angeschlossen ist;
d) gleichzeitig mit Schritt c), Extrudieren eines geschmolzenen herkömmlichen Polymers durch den Extrusionsring, wodurch ein Kunststoffrohres ausgebildet wird, in dem gleichzeitig aufgrund der Schwerkraft die endgültige pyrotechnische Mischung innerhalb des gebildeten Kunststoffrohres dosiert wird, wodurch das funkenerzeugende Rohr erhalten wird.

Revendications

1. Tube générant une étincelle, **caractérisé par** un mélange pyrotechnique adhérant à une paroi intérieure d'un tube en plastique comprenant les substances en poudre suivantes :

a) de 32% à 60% d'un carburant en poudre ou d'une substance réductrice qui génère une étincelle à haute température, choisi parmi les éléments du groupe formé de l'aluminium, du magnésium, du silicium, du bore et du zirconium ;
b) de 15% à 35% d'une substance qui génère des produits ayant une conduction thermique élevée et/ou des propriétés de convection, choisie parmi les éléments du groupe formé de l'oxyde magnétique - Fe_3O_4, de l'oxyde ferrique - Fe_2O_3, de l'oxyde ferreux - FeO, de l'oxyde de cobalt - CoO, de l'oxyde cuivrique - CuO et de l'oxyde cuivreux - Cu_2O ;
c) de 20% à 40% d'une substance réduisant l'énergie d'activation de la réaction pyrotechnique et générant des produits gazeux ayant un volume suffisamment grand pour se propager à travers les recoins, noeuds ou restrictions du tube, choisie parmi les éléments du groupe formé du perchlorate de potassium - $KClO_4$, du chlorate de potassium, du nitrate de potassium, du perchlorate d'ammonium, du perchlorate de sodium, du soufre et du trisulfure d'antimoine ;
d) de 0,5% à 3,0% d'une substance favorisant l'adhérence et réduisant la sensibilité au choc et à la friction du mélange pyrotechnique, choisie parmi les éléments du groupe formé du talc ou du graphite.

2. Tube selon la revendication 1, **caractérisé en ce que** la formulation optimisée du mélange pyrotechnique de celle-ci comprend :

a. de 32% à 60% d'aluminium en poudre ;

b. de 15% à 35% d'oxyde ferreux-ferrique - Fe_3O_4, en poudre ;
c. de 20% à 40% de perchlorate de potassium - $KClO_4$;
d. de 0,5% à 3,0% de talc.

3. Procédé de production d'un tube générant une étincelle, selon la revendication 1, comprenant les étapes de :

a) bien mélanger:

une substance choisie parmi les éléments du groupe a) tel qu'il est défini dans la revendication 1 et
une substance choisie parmi les éléments du groupe b) tel qu'il est défini dans la revendication 1
une substance choisie parmi les éléments du groupe c) tel qu'il est défini dans la revendication 1
pour former ainsi un mélange (1) ;

b) introduire ledit mélange (1) dans un premier silo de dosage et les substances d) de la revendication 1 dans un second silo de dosage ;
c) doser de façon continue des proportions équilibrées dudit mélange (1) et desdites substances d) de la revendication 1 avec deux appareils parallèles de dosage du type à vis ou avec des doseurs vibrants ou tout autre moyen conventionnel de microdosage par pesage ou volumétrique, équipés de moteurs électriques à régulation de fréquence ou tout autre régulateur conventionnel, dans une boucle de régulation avec une extrudeuse de tube en plastique, lesdites proportions équilibrées dosées atteignant de façon continue un rouleau homogénéisateur-mélangeur comportant une grille de fond, pour fabriquer ainsi le mélange pyrotechnique sensible final, ladite grille de fond étant reliée à un anneau d'extrusion de ladite extrudeuse de tube en plastique ;
d) simultanément avec l'étape c), extruder un polymère conventionnel fondu par ledit anneau d'extrusion pour former ainsi un tube en plastique et doser ainsi simultanément, par gravité, le mélange pyrotechnique final à l'intérieur du tube en plastique en train d'être formé pour obtenir ainsi le tube générant une étincelle.

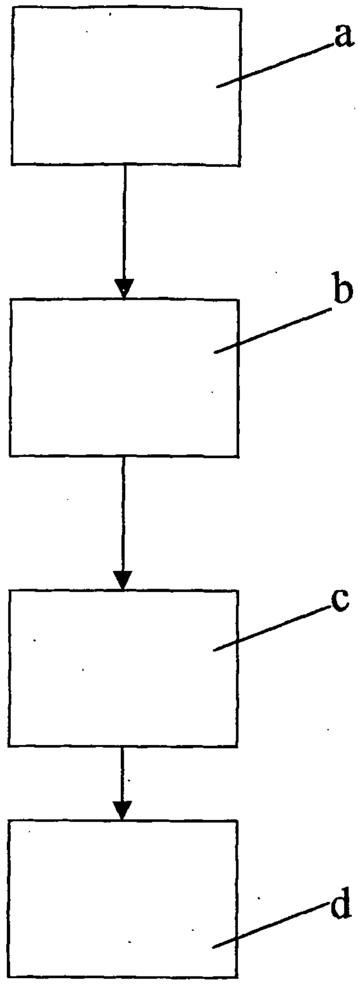

Fig. 1

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 3590739 A **[0003]**
- US 4328753 A **[0003]**
- EP 027219 A **[0003] [0003]**
- US 5317974 A **[0003]**
- US 5509355 A **[0003]**
- US 5166470 A **[0003]**
- BR PI8104552 **[0005] [0009]**
- US 4757764 A **[0005] [0010]**
- US 5173569 A **[0008]**
- US 5435248 A **[0008]**
- US 5942718 A **[0008]**
- BR PI9502995 **[0008]**

Non-patent literature cited in the description

- *28th. Annual conference of the ISEE,* 2002 **[0008]**