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(54) EXPLOSIVE COMPOSITIONS CONTAINING GLYCERIN

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(57) ABSTRACT

Glycerin-containing explosive compositions comprising at least an oxidizer and glycerin are provided. The explosive compositions may comprise a glycerin, such as impure or crude glycerin, modified crude glycerin, substantially pure glycerin or pure glycerin. The explosive compositions may comprise other combustible fuels such as fuel oil or carbonaceous material(s). The explosive compositions may be prepared on site, loaded in bulk on mobile platforms, and/or prepared and packaged in suitable containers.

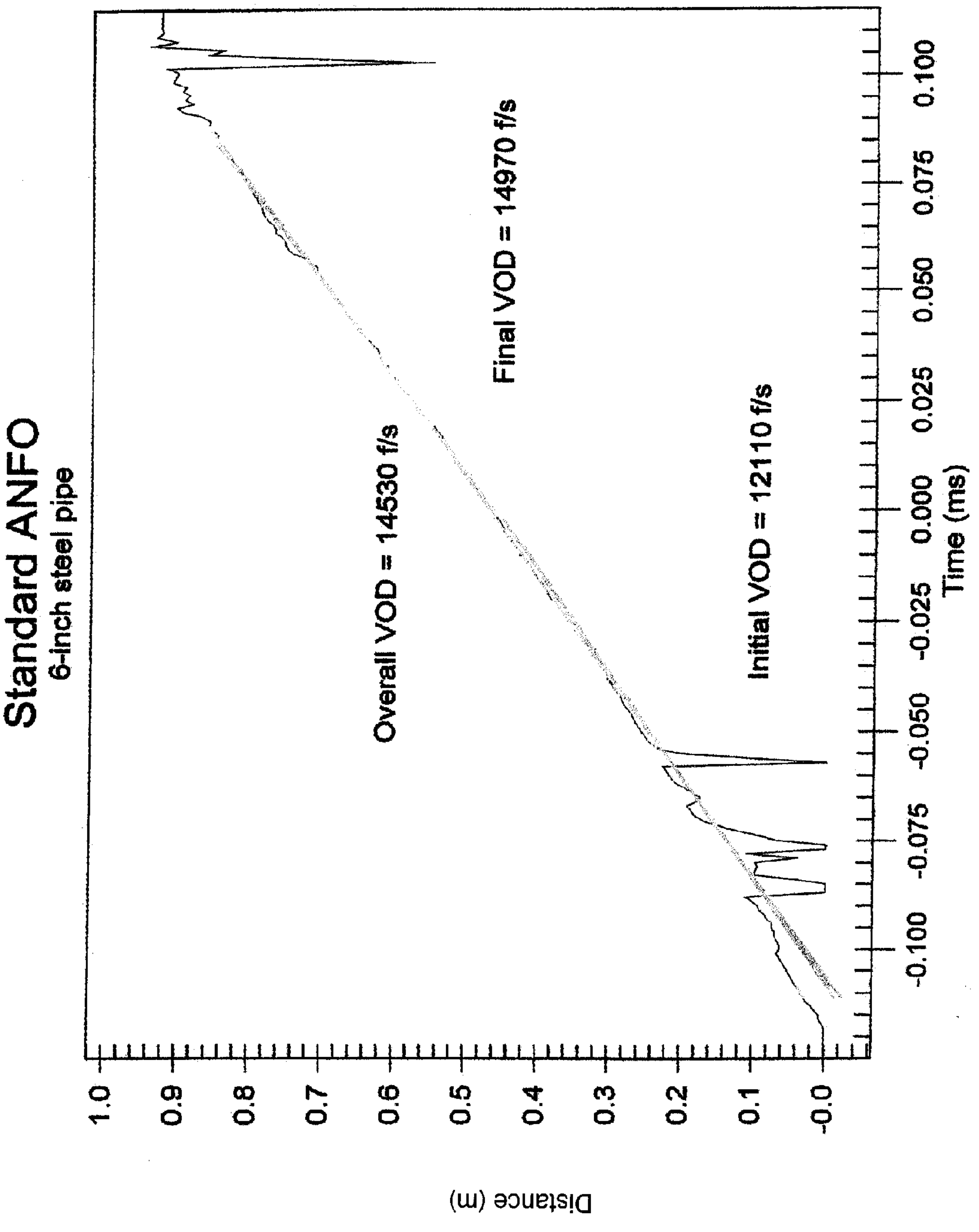

Standard ANFO
6-inch steel pipe
Overall VOD = 14530 f/s
Final VOD = 14970 f/s
Initial VOD = 12110 f/s
Distance (m)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-0.0
Time (ms)
-0.100
-0.075
-0.050
-0.025
0.000
0.025
0.050
0.075
0.100

FIGURE 1

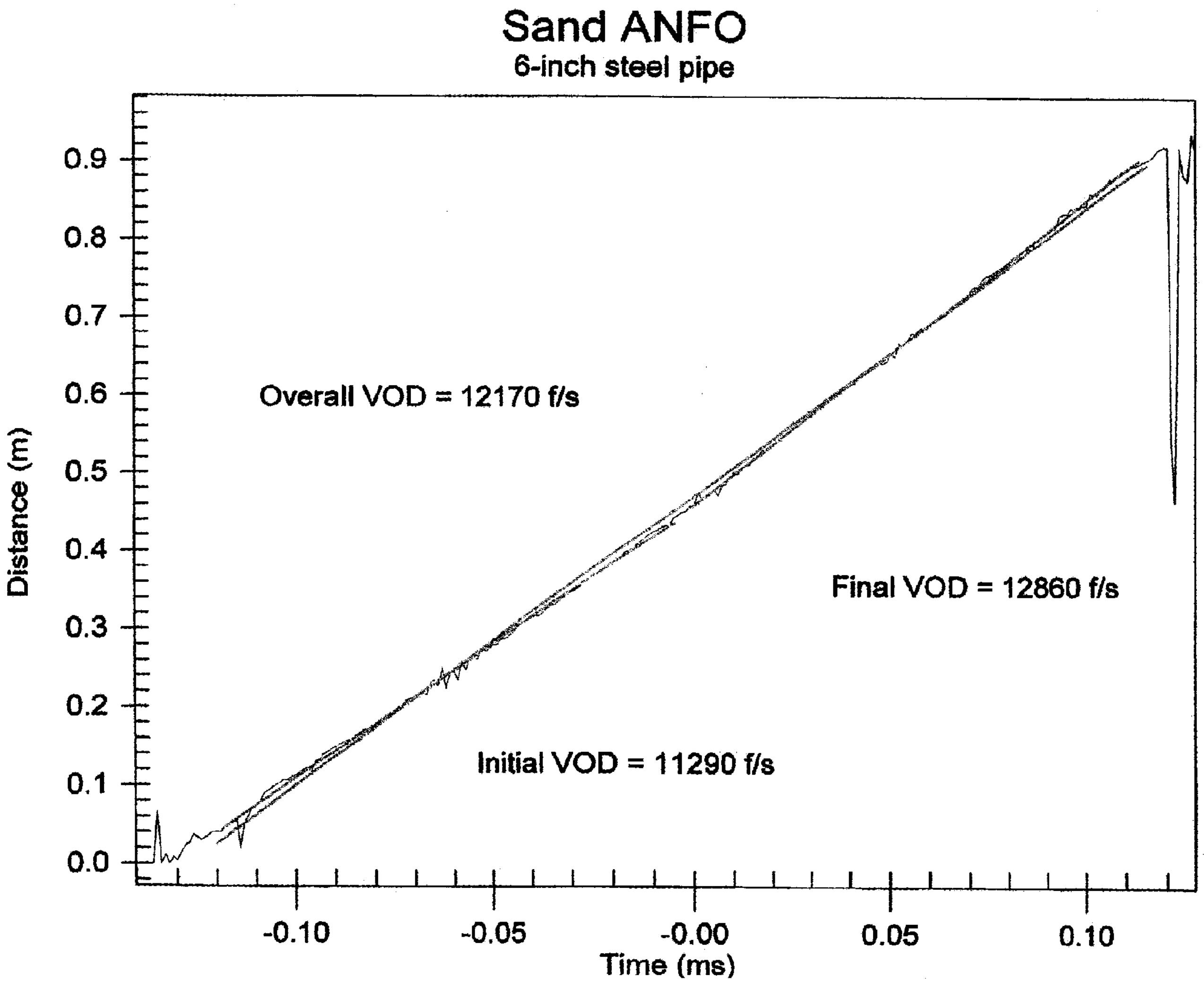

Sand ANFO
6-inch steel pipe
Distance (m)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Overall VOD = 12170 f/s
Final VOD = 12860 f/s
Initial VOD = 11290 f/s
-0.10
-0.05
-0.00
0.05
0.10
Time (ms)

FIGURE 2

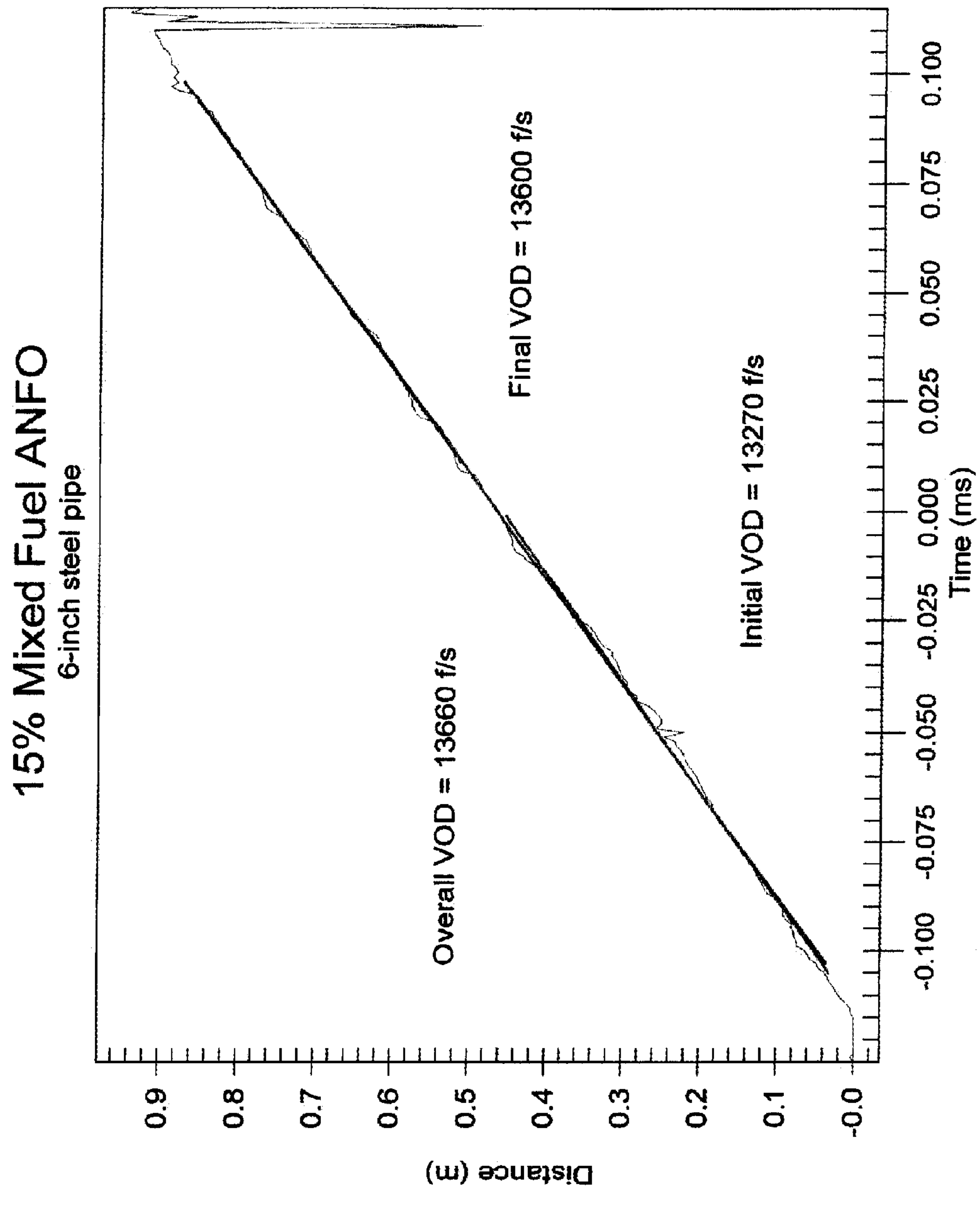

15% Mixed Fuel ANFO
6-inch steel pipe
Overall VOD = 13660 f/s
Final VOD = 13600 f/s
Initial VOD = 13270 f/s
Distance (m)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-0.0
-0.100
-0.075
-0.050
-0.025
0.000
0.025
0.050
0.075
0.100
Time (ms)

FIGURE 3

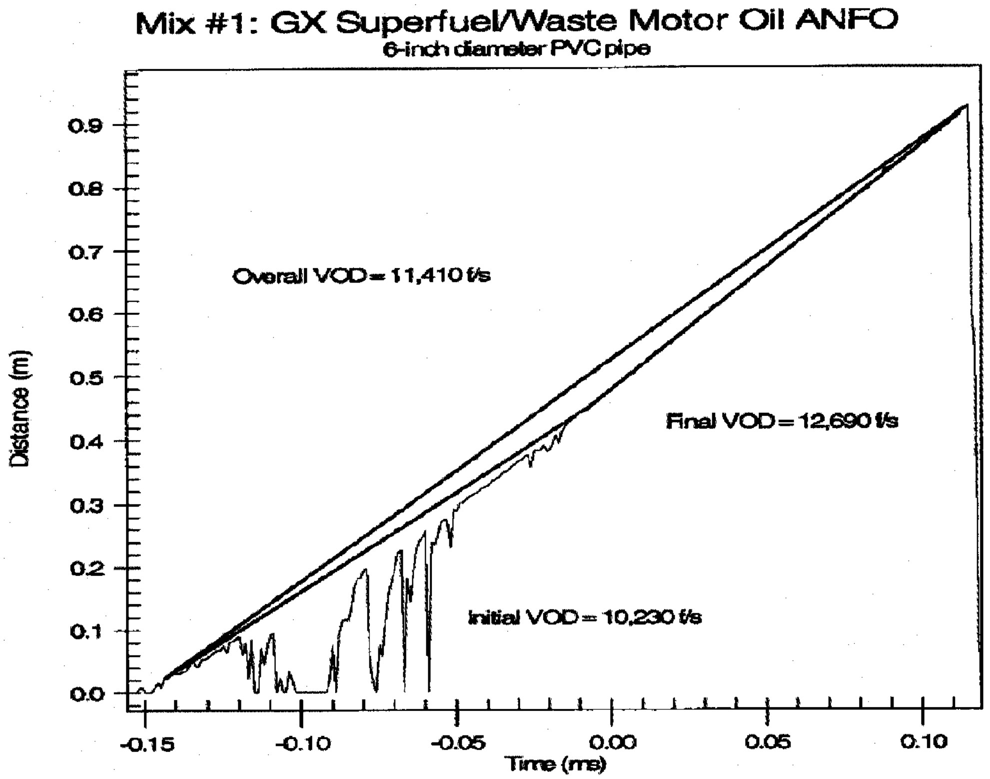

Mix #1: GX Superfuel/Waste Motor Oil ANFO
6-inch diameter PVC pipe
Overall VOD = 11,410 f/s
Final VOD = 12,690 f/s
Initial VOD = 10,230 f/s
Distance (m)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
-0.15
-0.10
-0.05
0.00
0.05
0.10
Time (ms)

FIGURE 4

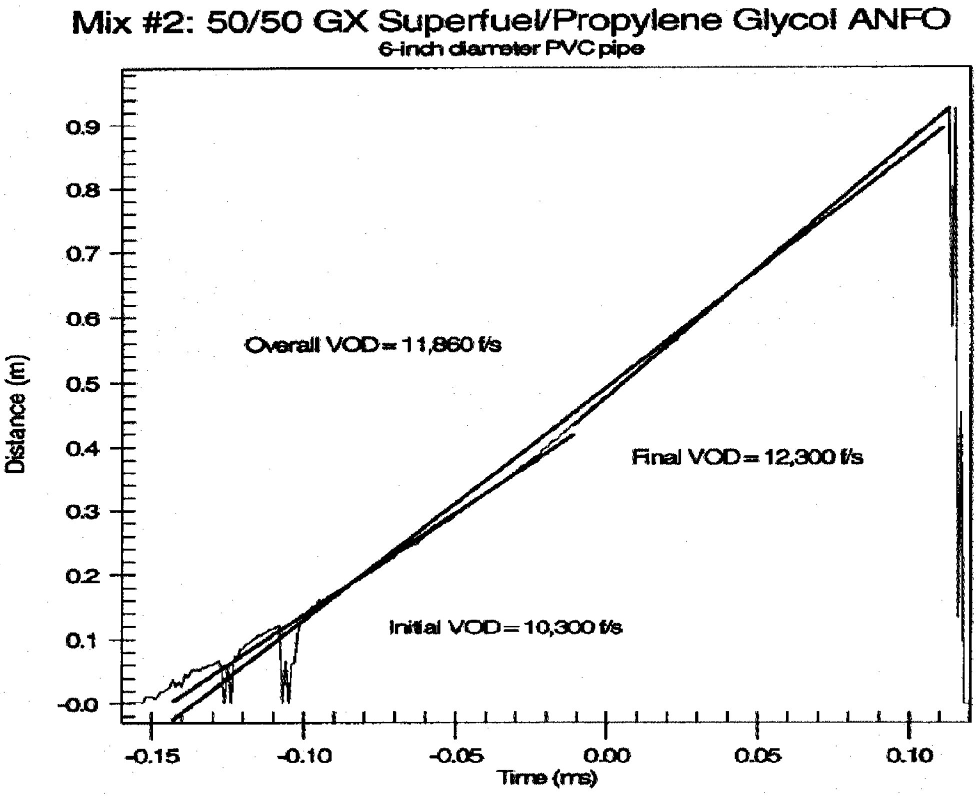
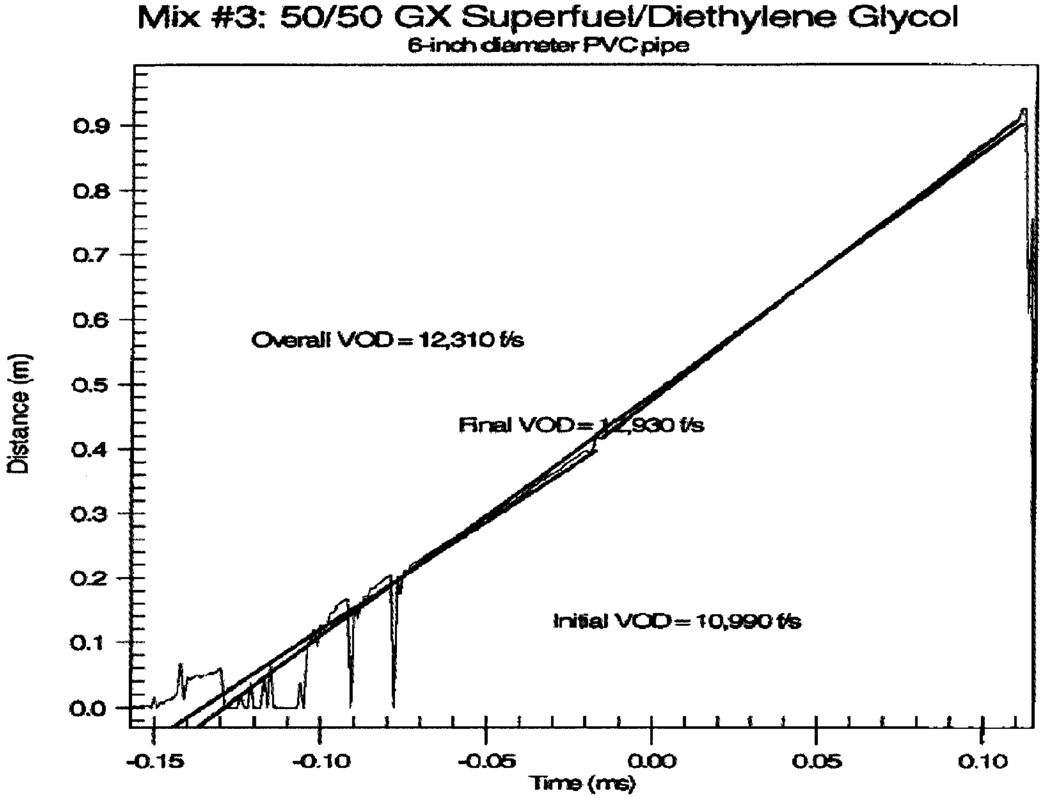

Mix #2: 50/50 GX Superfuel/Propylene Glycol ANFO
6-inch diameter PVC pipe
Distance (m)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-0.0
Overall VOD = 11,860 f/s
Final VOD = 12,300 f/s
Initial VOD = 10,300 f/s
-0.15
-0.10
-0.05
0.00
0.05
0.10
Time (ms)

FIGURE 5


Mix #3: 50/50 GX Superfuel/Diethylene Glycol

6-inch diameter PVC pipe

FIGURE 6

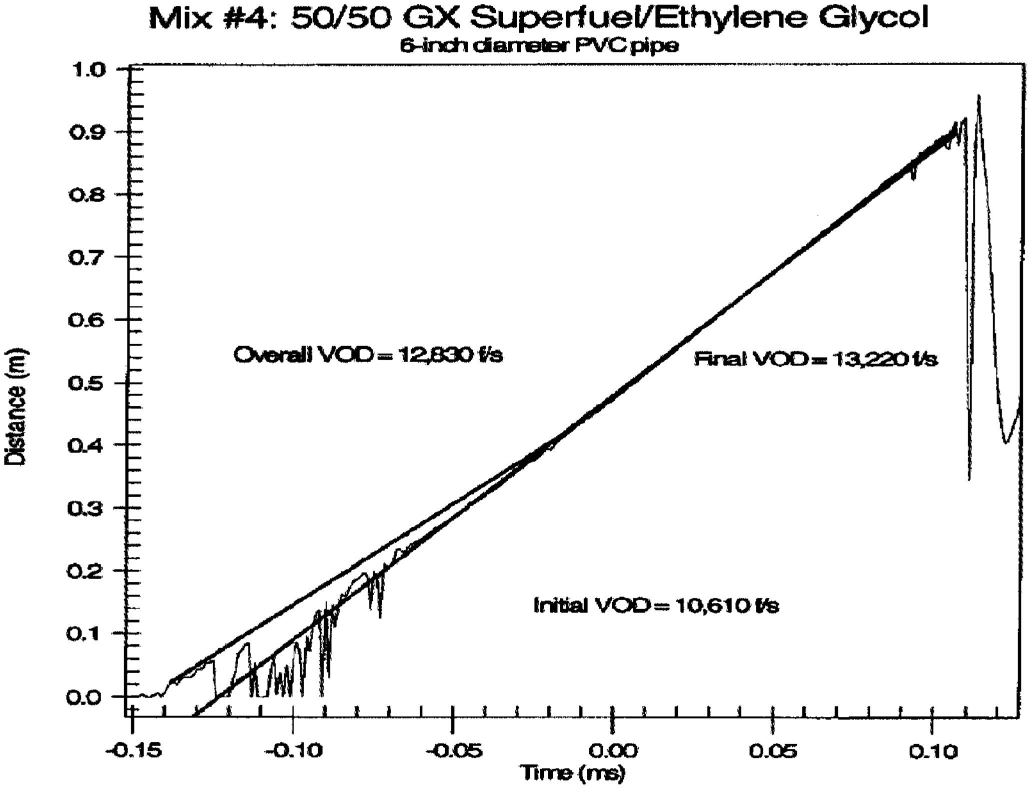

Mix #4: 50/50 GX Superfuel/Ethylene Glycol
6-inch diameter PVC pipe
Distance (m)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Overall VOD = 12,830 f/s
Final VOD = 13,220 f/s
Initial VOD = 10,610 f/s
-0.15
-0.10
-0.05
0.00
0.05
0.10
Time (ms)

FIGURE 7

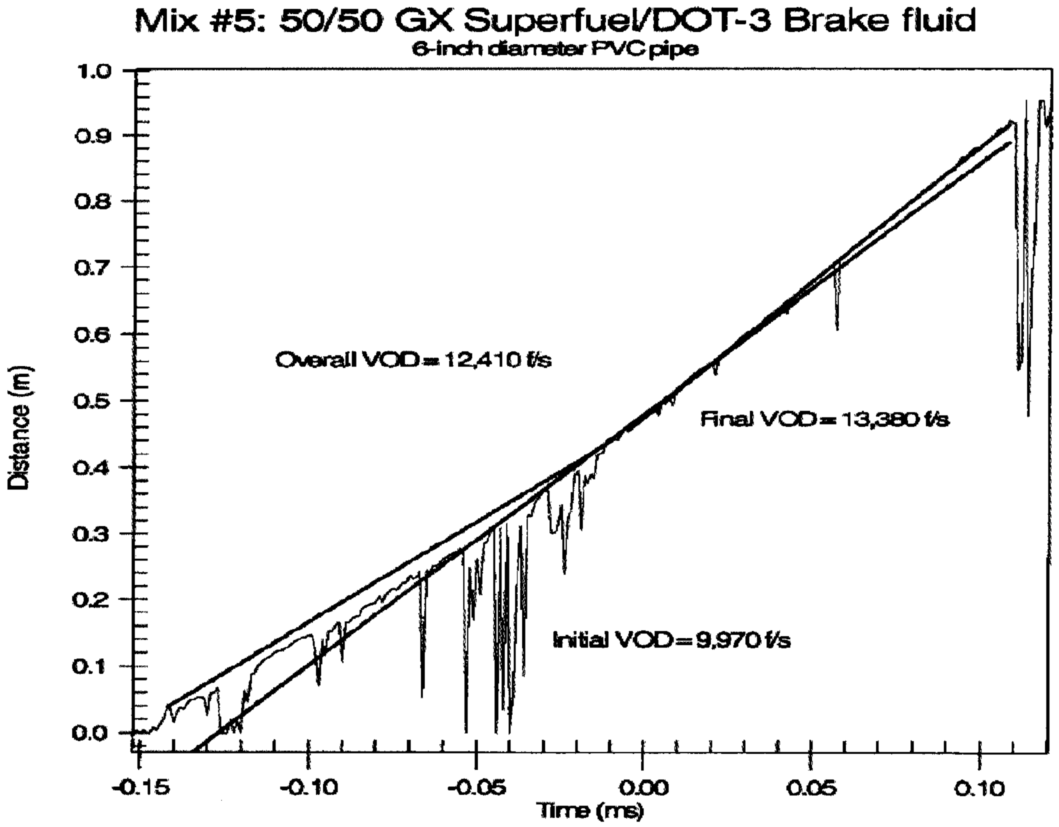

Mix #5: 50/50 GX Superfuel/DOT-3 Brake fluid
6-inch diameter PVC pipe
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Distance (m)
Overall VOD = 12,410 f/s
Final VOD = 13,380 f/s
Initial VOD = 9,970 f/s
-0.15
-0.10
-0.05
0.00
0.05
0.10
Time (ms)

FIGURE 8

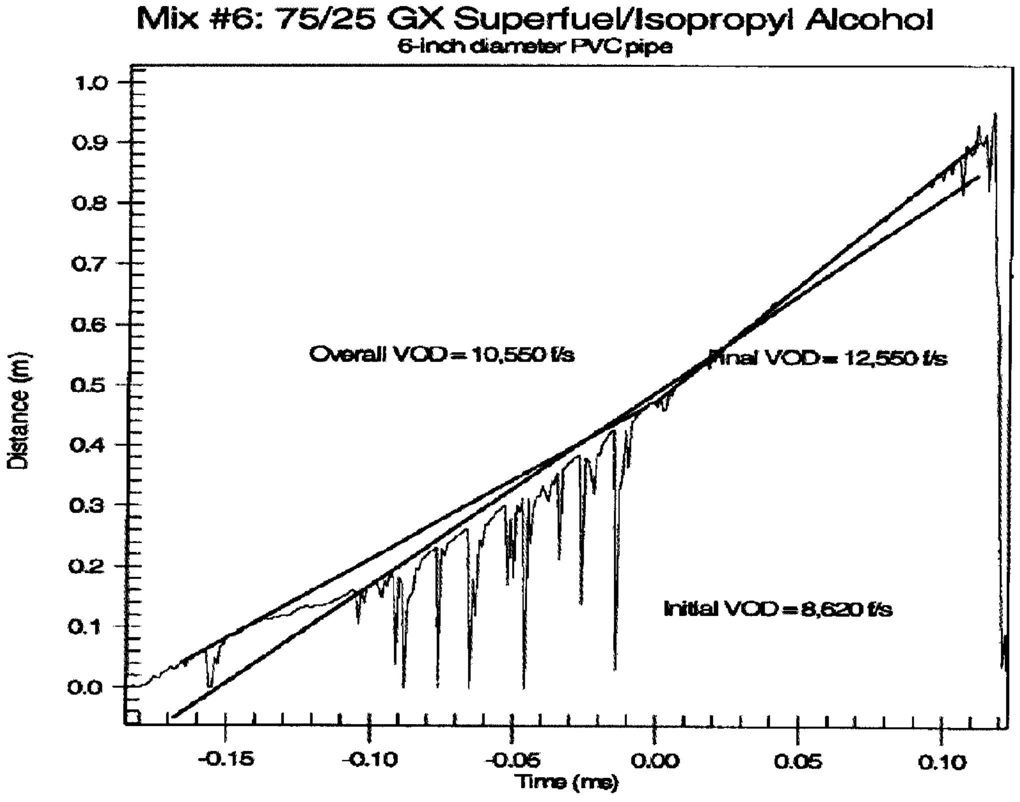

Mix #6: 75/25 GX Superfuel/Isopropyl Alcohol
6-inch diameter PVC pipe
Distance (m)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Overall VOD = 10,550 f/s
Final VOD = 12,550 f/s
Initial VOD = 8,620 f/s
-0.15
-0.10
-0.05
0.00
0.05
0.10
Time (ms)

FIGURE 9

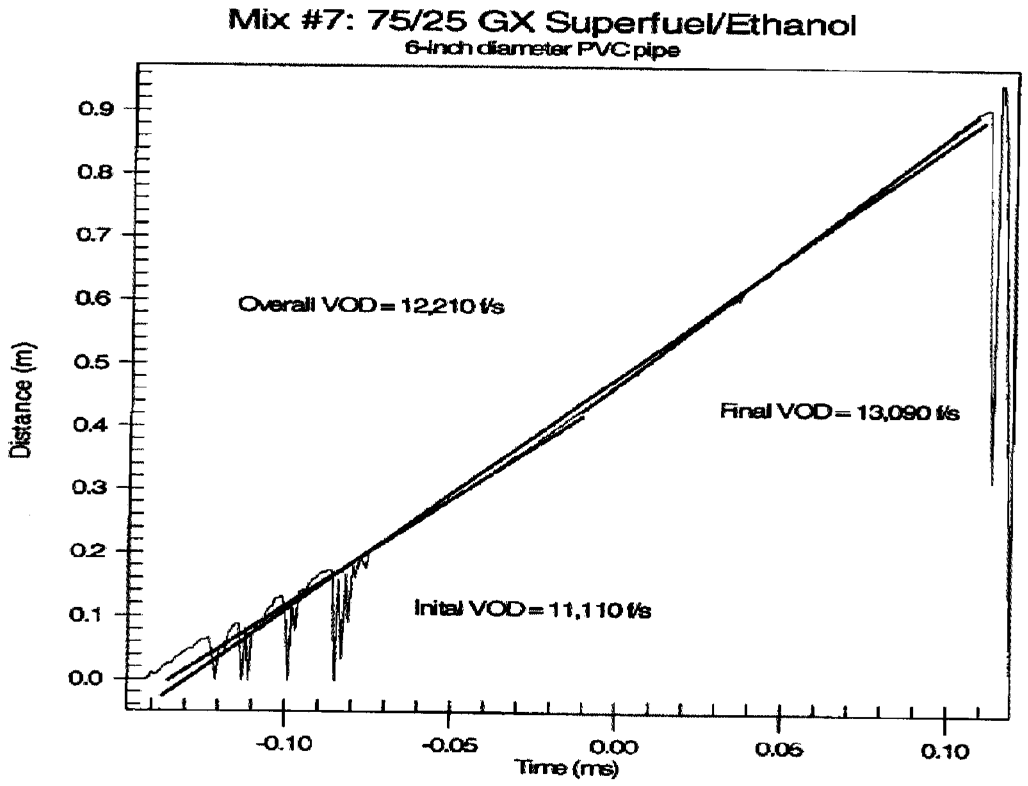

Mix #7: 75/25 GX Superfuel/Ethanol
6-inch diameter PVC pipe
Overall VOD = 12,210 ft/s
Final VOD = 13,090 ft/s
Initial VOD = 11,110 ft/s
Distance (m)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.10
-0.05
0.00
0.05
0.10
Time (ms)

FIGURE 10

EXPLOSIVE COMPOSITIONS CONTAINING GLYCERIN

PRIORITY DATA

[0001] This application claims priority under 35 U.S.C. §119 to Provisional Patent Application No. 60/886,190 filed on Jan. 23, 2007.

FIELD OF THE INVENTION

[0002] This application relates to explosive compositions comprising at least an oxidizer and glycerin and methods of using explosive compositions.

BACKGROUND

[0003] In 1956, a new blasting agent using the mixture of ammonium nitrate, aluminum powder, and water was developed. The safety and efficiency of this new explosive was apparent, and the use of water was revolutionary. Tests that followed resulted in the development of a new field of explosives: slurry explosives. This development converted the commercial explosives industry from "dangerous dynamite" to "safe slurry" and dry blasting agents. In 1972, Melvin A. Cook developed the BLU-82, the largest and most powerful chemical bomb, using aluminized slurry.

[0004] Blasting agents contain mixtures of fuels and oxidizers, none of which are classified as explosive. Nitrocarbonitrate is a classification given to a blasting agent under the U.S. Department of Transportation regulations on packaging and shipping. A blasting agent contains inorganic nitrates and carbonaceous fuels and may contain additional nonexplosive substances such as powdered aluminum or ferrosilicon to increase density. The addition of an explosive ingredient such as TNT changes the classification from a blasting agent to an explosive. Blasting agents may be dry or in slurry forms. Because of their insensitivity, blasting agents should be detonated by a primer of high explosive.

[0005] Today, ammonium nitrate-fuel oil (ANFO) blasting agents represent the largest industrial explosive manufactured (in terms of quantity) in the United States. This product is used primarily in mining and quarrying operations. The components are generally mixed at or near the point of use for safety reasons. The mixed product is relatively safe and easily handled and can be poured into drill holes in the mass or object to be blasted. ANFO has largely replaced dynamites and gelatins in bench blasting. Denser slurry blasting agents are supplanting dynamite and gelatin and dry blasting agents. The most widely used dry blasting agent is a mixture of ammonium nitrate prills (porous grains) and fuel oil.

[0006] The basic chemistry of ANFO detonation is the reaction of ammonium nitrate (NH_4NO_3) with a long chain hydrocarbon (CnH2n2+) to form nitrogen, carbon dioxide and water. The products of the reaction are the desirable gases of detonation, although some CO and NO_2 are always formed. Weight proportions of ingredients for the equation are 94.5 percent ammonium nitrate and 5.5 percent fuel oil. In actual practice the proportions are 94 percent and 6 percent to assure an efficient chemical reaction of the nitrate. When detonation conditions are optimal, the aforementioned gases are the only products. In practical use, such conditions are impossible to attain, and blasts produce moderate amounts of toxic gases such as carbon monoxide, hydrogen sulfide, and oxides of nitrogen (NO_x). The fuel oil is not precisely CH_2, but this is sufficiently accurate to characterize the reaction.

[0007] Uniform mixing of oil and ammonium nitrate is generally important for the development of a full explosive force. Some blasting agents are premixed and packaged by the manufacturer. Where not premixed, several methods of mixing in the field can be employed to achieve uniformity. The best method, although not always the most practical one, is by mechanical tier. A more common and almost as effective method of mixing is by uniformly soaking prills in opened bags with 8 to 10 percent of their weight of oil. After draining for at least a half hour the prills will have retained about the correct amount of fuel oil.

[0008] Fuel oil may also be poured onto the ammonium nitrate in approximately the correct proportions as it is poured into the blasthole. For this purpose, about 1 gallon of fuel oil for each 100 pounds of ammonium nitrate will equal approximately 6 percent by weight of oil. The oil may be added after each bag or two of prills, and it will disperse relatively rapidly and uniformly. Inadequate priming generally imparts a low initial detonation velocity to a blasting agent, and the reaction may die out and cause a misfire. High explosive boosters are sometimes spaced along the borehole to assure propagation throughout the column.

[0009] As in other combustion reactions, a deficiency of oxygen favors the formation of carbon monoxide and unburned organic compounds and produces little, if any, nitrogen oxides. An excess of oxygen causes more nitrogen oxides and less carbon monoxide and other unburned organics. For ammonium nitrate and fuel oil mixtures, a fuel oil content of more than 5.5 percent creates a deficiency of oxygen.

[0010] Ammonium nitrate and fuel oil have a broad spectrum of Velocities of Detonation (VOD) according to numerous references. However, some of these references are more specific when establishing parameters. A military cratering charge lists a VOD of 10,700 feet per second (fps). A 4" diameter steel tube confinement is at 10,000 fps, while a 16" diameter tube is at 16,000 fps. In charge diameters of 6 in. or more, dry blasting agents attain confined detonation velocities of more than 12,000 fps, but in a diameter of 1½ in., the velocity is reduced to 60 percent. Enhanced effects are obtained with very large quantities, which are essentially self-tamping: the VOD is expected to be in the 13,000-15,000 fps range. An approximation for very large quantities of blasting agents, which is accepted in the commercial industry, is roughly half the VOD of C-4 plastics, which equates to 13,000 fps. The recognized VOD of urea nitrate, however, is 11,155 to 15,420 fps.

[0011] In addition to fuel oil or long chain hydrocarbons as the fuel phase, other carbonaceous materials have been utilized to make ANFO type explosives, which have included various cellulosic materials, glycol still bottoms, various polymeric foams such as polystyrene beads and coal dust, any of which or a combination of which may be used in the explosive compositions provided herein, as described below. All these blends have shown some limitations and generally lower VOD and detonation performance overall.

[0012] The specific gravity of ANFO varies from 0.75 to 0.85 depending on the particle density and sizes of the prills, with the amount of fine ammonium nitrate powder from broken down prills being the most significant element generating the high densities. In fact, most of the additives utilized in the preferred embodiments described hereinafter result in lower ANFO density as a result of their large particle size and inherent density. Confined detonation velocity and charge concentration of ANFO vary with borehole diameter. Pneumatic loading results in high detonation velocities and higher charge concentrations, particularly in holes smaller than 3 inches (otherwise such small holes are not usually recommended for ANFO blasting).

[0013] The simple removal of a tree stump might be done with a 2-step train made up of an electric blasting cap and a stick of dynamite. The detonation wave from the blasting cap would cause detonation of the dynamite. To make a large hole in the earth, an inexpensive explosive such as ANFO might be used. In this case, the detonation wave from the blasting cap is not powerful enough to cause detonation, so a booster must be used in a 3- or 4-step train. The yield from the blasting caps and safety fuses used in these trains are usually small compared to those from the main charge, because the yields are roughly proportional to the weight of explosive used, and the main charge makes up most of the total weight.

[0014] Advantages of insensitive dry blasting agents are their safety, ease of loading, and low price. In the free-flowing form, they have a great advantage over cartridge explosives because they completely fill the borehole. This direct coupling to the walls assures efficient use of explosive energy. Ammonium nitrate is water-soluble so that in wet holes, some blasters pump the water from the hole, insert a plastic sleeve, and load the blasting agent into the sleeve. Special precautions should be taken to avoid a possible building up of static electrical charge, particularly when loading pneumatically. When properly oxygen-balanced, the fume qualities of dry blasting agents permit their use underground. Canned blasting agents, once widely used, have unlimited water resistance, but lack advantages of loading ease and direct coupling to the borehole.

[0015] Engineers in the Fuels and Lubricants Group of Shell Co. of Australia developed a technique to blend waste oil with ANFO for a product that can be used in blasting. Mines throughout the world produce thousands of liters of waste fuel oil that needs to be disposed of in an environmentally safe manner. By using the fuel oil in a blasting compound, transporting the waste oil is eliminated, the quantity of fuel oil needed for blasting is reduced, and the high blast temperature can destroy potentially toxic hydrocarbons in waste oil. Shell tested the ANFO-waste oil blend at Hamersley Iron's Marandoo mine site, and found that the ratio of waste oil to ANFO blend could be as much as 50-50 without any detrimental effect to the final blasting performance; however, no data was available on the amount of absorbed/adsorbed oil versus the oil that drained and pooled to the bottom of the hole, so the 50/50 ratio may be optimistic.

[0016] Glycerin is a major byproduct from the manufacture of biodiesel from agricultural materials. It would be desirable to provide a glycerin fueled explosive composition that utilizes glycerin as a fuel. Also desirable would be to provide an explosive composition that employs glycerin derived from a biomass fuel source, such as impure or crude glycerin which is produced as a byproduct of biodiesel production. It further would be appealing to provide an explosive composition that uses a combination of impure or crude glycerin and other fuel, such as organic fuels, waste oil and/or fuel oil.

[0017] Throughout this description, including the foregoing description of related art, any and all publicly available documents described herein, including any and all U.S. patents, are specifically incorporated by reference herein in their entirety. The foregoing description of related art is not intended in any way as an admission that any of the documents described therein, including pending United States patent applications, are prior art to the present invention. Moreover, the description herein of any disadvantages associated with the described products, methods, and/or apparatus, is not intended to limit the invention. Indeed, aspects of the invention may include certain features of the described products, methods, and/or apparatus without suffering from their described disadvantages.

SUMMARY

[0018] An explosive composition comprising a glycerin and at least one oxidizer is provided in an embodiment.

[0019] An explosive composition comprising a glycerin, at least one oxidizer, and at least one non-glycerin combustible fuel is provided in another embodiment.

[0020] An explosive composition comprising a glycerin and ammonium nitrate is provided in a further embodiment.

[0021] An explosive composition comprising a glycerin, ammonium nitrate, and a non-glycerin combustible fuel oil is provided in an embodiment.

[0022] An explosive composition comprising crude glycerin derived from a biomass fuel source and at least one oxidizer is provided in a further embodiment.

[0023] An explosive composition comprising crude glycerin derived from a biomass fuel source, at least one oxidizer, and at least one non-glycerin combustible fuel is provided in another embodiment.

[0024] A packaged blasting agent comprising an explosive composition, wherein the explosive composition comprises a glycerin and ammonium nitrate, wherein said explosive composition is contained in a water-resistant package or is coated with a water-blocking agent is provided in an embodiment.

[0025] A packaged blasting agent comprising an explosive composition, wherein the explosive composition comprises a glycerin, ammonium nitrate, and a non-glycerin combustible fuel oil, and wherein said explosive composition is contained in a water-resistant package or is coated with a water-blocking agent is provided in an embodiment.

[0026] A packaged blasting agent comprising an explosive composition, wherein the explosive composition comprises crude glycerin derived from a biomass fuel source and ammonium nitrate, wherein said explosive composition is contained in a water-resistant package or is coated with a water-blocking agent is provided in another embodiment.

[0027] A packaged blasting agent comprising an explosive composition, wherein the explosive composition comprises crude glycerin derived from a biomass fuel source, ammonium nitrate, and a non-glycerin combustible fuel oil, and wherein said explosive composition is contained in a water-resistant package or is coated with a water-blocking agent is provided in an embodiment.

[0028] An explosive composition prepared from a method comprising combining a glycerin and a solid inorganic oxidizer is provided in a another embodiment.

[0029] An explosive composition prepared from a method comprising combining a glycerin, a solid inorganic oxidizer, and a non-glycerin combustible fuel is provided in a further embodiment.

[0030] An explosive composition prepared by a method comprising combining crude glycerin derived from a biomass fuel source and a solid inorganic oxidizer is provided in yet another embodiment.

[0031] An explosive composition prepared by a method comprising combining crude glycerin derived from a biomass fuel source, a solid inorganic oxidizer, and a non-glycerin combustible fuel is provided in another embodiment.

[0032] A method for preparing an explosive composition comprising combining a glycerin and a solid inorganic oxidizer is provided in an embodiment.

[0033] A method for preparing an explosive composition comprising combining a glycerin, a solid inorganic oxidizer, and at least one non-glycerin combustible fuel is provided in another embodiment.

[0034] A method for preparing an explosive composition comprising combining a crude glycerin derived from a biomass fuel source and ammonium nitrate is provided in a further embodiment.

[0035] A method for preparing an explosive composition comprising combining a crude glycerin derived from a biomass fuel source, ammonium nitrate, and a non-glycerin combustible fuel oil is provided in an embodiment.

[0036] Also provided is a method of using an explosive composition comprising providing any of the explosive compositions provided herein, loading said explosive composition into a blast hole and detonating the explosive composition.

[0037] Further provided is a method of using an explosive composition comprising loading any of the explosive compositions provided herein into a blast hole and detonating the explosive composition.

[0038] These and other embodiments will become readily apparent to those skilled in the art upon review of the detailed description that follows.

BRIEF DESCRIPTION OF DRAWINGS

[0039] FIG. **1** shows the VOD traces resulting from the unconfined VOD test of Example 4 for the standard ANFO mix (09-1 mix) using 6-inch diameter steel pipe.

[0040] FIG. **2** shows the VOD traces resulting from the unconfined VOD test of Example 4 for the 3% FO/7% Sand ANFO mix (09-4 mix) using 6-inch diameter steel pipe.

[0041] FIG. **3** shows the VOD traces resulting from the unconfined VOD test of Example 4 for the 15% Glycerin ANFO mix (13-2) using 6-inch diameter steel pipe.

[0042] FIG. **4** shows the VOD traces resulting from the unconfined VOD test of Example 6 for the GX Superfuel/Waste Motor Oil ANFO mix (Mix #1) using 6-inch diameter PVC pipe.

[0043] FIG. **5** shows the VOD traces resulting from the unconfined VOD test of Example 6 for the 50/50 GX Superfuel/Propylene Glycol ANFO mix (Mix #2) using 6-inch diameter PVC pipe.

[0044] FIG. **6** shows the VOD traces resulting from the unconfined VOD test of Example 6 for the 50/50 GX Superfuel/Diethylene Glycol ANFO mix (Mix #3) using 6-inch PVC pipe.

[0045] FIG. **7** shows the VOD traces resulting from the unconfined VOD test of Example 6 for the 50/50 GX Superfuel/Ethylene Glycol ANFO mix (Mix #4) using 6-inch PVC pipe.

[0046] FIG. **8** shows the VOD traces resulting from the unconfined VOD test of Example 6 for the 50/50 GX Superfuel/DOT-3 Brake fluid ANFO mix (Mix #5) using 6-inch PVC pipe.

[0047] FIG. **9** shows the VOD traces resulting from the unconfined VOD test of Example 6 for the 75/25 distilled GX Superfuel/Isopropyl Alcohol ANFO mix (Mix #6) using 6-inch PVC pipe.

[0048] FIG. **10** shows the VOD traces resulting from the unconfined VOD test of Example 6 for the 75/25 GX Superfuel/Ethanol ANFO mix (Mix #7) using 6-inch PVC pipe.

DETAILED DESCRIPTION OF THE INVENTION

[0049] For the purposes of promoting an understanding of the embodiments described herein, reference will be made to embodiments and specific language will be used to describe the same. The terminology used herein is for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention. As used throughout this disclosure, the singular forms “a,” “an,” and “the” include plural reference unless the context clearly dictates otherwise. Thus, for example, a reference to “a composition” includes a plurality of such compositions, as well as a single composition.

[0050] The explosive compositions of the embodiments comprises an explosive mixture of at least a solid inorganic oxidizer and a glycerin, hereinafter referred to as a “glycerin fueled explosive composition.” A “glycerin” as used herein, is defined as a composition of glycerin wherein the composition may include an amount of glycerin from as low as at least 7% to 13% glycerin, i.e., an impure glycerin, to an amount of 99% pure glycerin or higher pure glycerin. The term “glycerin” also is defined to include a composition which is comprised of entirely glycerin, and is also known as 100% glycerol, i.e., the alcohol. An “impure glycerin” also referred to herein as a “crude glycerin” is defined as a glycerin composition which comprises (a) at least 7% to 13% glycerin up to 50% glycerin or higher percentage of glycerin, and (b) an impurity, includes but is not limited to, an alcohol, such as methanol (or other alcohols), salts, fatty acids, salts of fatty acids, unused catalyst, such as caustic material, e.g., an alkali hydroxide (e.g., from a biodiesel production process), neutralizing acids, including but not limited to, citric acid, sulfuric acid, hydrochloric acid, acetic acid, tartaric acid or ascorbic acid, foaming agents, excess water, as well as traces of proteins, solids and other naturally occurring materials, which are the source of the glycerin production (e.g., biomass, which may be degraded as a result of the process which produces the impure glycerin) and remain in the waste stream of the process which produces the impure glycerin, or combinations thereof of any such impurities. A glycerin may be derived from a process of transesterification of biomass fuel sources, such as plant and animal oils, which transesterification produces impure glycerin and biodiesel. As used herein “derived from” means to be obtained from, through, by or as a result of a process (such as transesterification or saponification); however, a “derived” glycerin, such as a glycerin derived from a process, may not be the sole or only result or product produced by or obtained from such a process.

[0051] A glycerin produced as a byproduct of biodiesel production is by definition an impure (or crude) glycerin and such impure glycerin may contain an excess of methanol, which may be removed by a flash evaporation process or by distillation. The glycerin, i.e., the biodiesel byproduct, may also contain unused catalyst (sodium hydroxide or potassium hydroxide), soaps and salts. Such a glycerin byproduct as used and defined herein is an “impure glycerin” or “crude glycerin.” Impure or crude glycerin may have salts remaining therein, or alternatively, may salts removed therefrom. The crude glycerin may be neutralized with an acid, e.g., acetic acid; such a modified glycerin is referred to herein as a “modified impure glycerin,” a “modified crude glycerin,” a “neutralized impure glycerin" or a "neutralized crude glycerin." In an embodiment, the impure or crude glycerin may be distilled to remove excess alcohol once the impure glycerin has been separated from the biodiesel phase. In another embodiment, the crude glycerin may be distilled and neutralized before the glycerin and the biodiesel are separated. In a further embodiment, neutralized crude glycerin may be distilled to a higher purity. Water and alcohol may be removed from the "impure glycerin" or the "crude glycerin," which then becomes 80-88% pure glycerin and this glycerin is defined, or referred to, herein as an "impure glycerin," a "crude glycerin" or a "substantially pure glycerin." Distillation of the 80-88% pure glycerin (which is still impure) produces a 99% pure glycerin or glycerin of a higher purity, and such a distilled glycerin, as used herein, also is defined, or referred to, herein as "substantially pure glycerin." Glycerin that is 100% pure alcohol, i.e., glycerol, is defined or referred to, herein as "pure" glycerin.

[0052] In an alternative embodiment, a glycerin may be derived from a process of saponification of triacylglycerides, such as soap making (or candle making from animal fats), in which fats and lye (sodium hydroxide or potassium hydroxide) react to produce glycerin blended within the mixture of soap, glycerin and impurities. A glycerin may be removed from this mixture by adding salt, removing the soap formed thereby, followed by distillation to separate the glycerin.

[0053] In an embodiment, a glycerin may be used as the predominant or sole fuel source. The glycerin may be derived from a biomass fuel source or a crude glycerin, which is derived from a biomass fuel production, e.g., biodiesel production, or derived from any process which results in impure or crude glycerin as a byproduct. The glycerin produced from a biomass fuel source may be modified by neutralization and/or distillation to produce substantially pure glycerin or pure glycerin. Glycerin may be present in the explosive composition in an amount of from at least about 7 wt %. Levels as high as 33% have been successfully used.

[0054] As is well known, an explosive composition performs closer to its theoretical maximum energy production if it is oxygen-balanced or nearly so. The oxygen balance of the glycerin fueled explosive composition of one embodiment ranges from about a +5 to about a −20. In some instances it may be desirable to add additional combustible fuel components such as carbonaceous combustible materials to glycerin fueled explosive mix in order to improve the efficiency of the explosive composition. The addition of at least one other combustible fuel may therefore be used to correct the "oxygen balance" of the glycerin fueled explosive composition.

[0055] The foregoing description of the fuel component typically used in the production of ANFO describes the use of long chain hydrocarbons, other carbonaceous material, and even glycol still bottoms, but the prior art was noticeably absent of highly oxygenated fuels like glycerin. The use of a highly oxygenated fuel like glycerin would traditionally not be a first choice when formulating a high VOD (properly detonating) ANFO; however, glycerin has been found to be a suitable replacement for the commonly used fuel oils in ANFO explosives, providing finished explosives preferably having VODs of about 14,000 to about 16,000 ft/s (fps), and detonation performance that surpasses conventional ANFO.

[0056] A further benefit of glycerin based ANFO has been its ability to increase the overall density of the finished explosive blend via (i) its own high density, (ii) its ability to fill the interstitial spaces between the prills, (iii) the moderate softening of the outer surface of prills and the resultant slight slumping and (iv) the different permeation mechanism into the AN prill. Typical loading densities of 1.05 g/cc have been utilized, with densities of as high as 1.18 g/cc being reliably used. The result of the higher densities is the increased powder factor which can be achieved over conventional ANFO, resulting in higher bulk strength for the product. This higher performance can be used to improve blasting results when using conventional patterns (fragmentation, heave, muck pile profile, digging efficiency), or it can be used to expand patterns over conventional ANFO.

[0057] The embodiments encompass explosive compositions comprising a mixture of at least one nitrate salt oxidizer and a glycerin used alone or diluted with water. Alternatively, the glycerin may be blended with other additives such as salts, water, alcohols, and thickeners, other organic compounds, hydrocarbons, cross-linkers and pH adjusters to form a matrix composition. This matrix composition can then be mixed with at least one nitrate salt oxidizer to form an explosive composition.

[0058] The glycerin may be provided from a variety of sources. For example, the source of the glycerin may be a byproduct from a manufacturing process. According to an embodiment, a source of glycerin is crude glycerin solution such as those glycerin solutions produced as byproduct from the manufacture of biodiesel from agricultural materials. Crude glycerin (and other polyols) may be derived from biomass fuels, e.g., by transesterification of fat or oil (e.g., a vegetable oil), as described above; such crude glycerin is referred to herein as a glycerin derived from a biomass fuel source. Biomass fuel sources include wood and forest residues, animal manure and waste, grains, plants, crops and aquatic plants. Crude glycerin may contain glycerin (50% to 100%), caustic material such as sodium hydroxide (up to 10%), methanol (0% to 50%), fatty acids and corresponding fatty acid salts (0% to 10%). In an embodiment, the crude glycerin may comprise up to 35% methanol, up to 10% caustic material, up to 5% fatty acids and fatty acid salts and other materials found in the waste stream of the process (e.g., neutralizing agents, excess water, foaming agents), which produces the impure glycerin. In another embodiment, the impure glycerin may comprise 0% to 23% methanol, 50% to 100% glycerin, 0% to 10% salts, 0% to 10% fatty acid and fatty acid salts and impurities (or contaminants) such as traces of proteins, solids and other materials naturally found in the sources from which the crude glycerin is derived.

[0059] One such crude glycerin solution is a GX Superfuel byproduct which is a solution of crude glycerin with a methanol content of about 30 percent. The glycerin may be a substantially pure glycerin, which may be derived from the processes described herein, e.g., transesterification or saponification, which processes use biomass fuel sources and/or result in crude glycerin as a byproduct. The glycerin also may be a pure glycerin, which has been derived from such a process, e.g., as a byproduct of biomass fuel production such as biodiesel production. In each of these embodiments the glycerin may be modified by neutralization and distillation, wherein modification by distillation may occur before neutralization, after neutralization or both, i.e., before and after neutralization.

[0060] Thus, according to another embodiment, a glycerin is used in combination with fuel oil or any other combustible fuel known to create a high explosive (detonation at rates from about 1,000 to about 9,000 meters per second) when mixed with a solid inorganic oxidizer (e.g., ammonium nitrite). Examples of combustible fuel that may be used in combination with glycerin include, but are not limited to, fuel oil, heating oil, diesel fuel, jet fuel, kerosene, waste motor oil, propylene glycol, diethylene glycol, ethylene glycol, brake fluid, including but not limited to, DOT-3 brake fluid and DOT-4 brake fluid, isopropyl alcohol, ethanol, any cellulosic material(s), low density cellulosic material(s), coal dust, coal powder and combinations and mixtures thereof. Low density cellulosic material, includes but is not limited to finely divided wood in the form of wood shavings or sawdust, as well as the cellulosic materials which are used to make any of: paper, tissue products such as napkins, or multi-ply articles such as plywood. Cellulosic material includes but is not limited to peanut shells or other type of nut shells, corn, corncobs, corn husks, puffed corn, puffed rice, rice hulls, fruit pits, bagasse, or any other material of plant origin, i.e., any biomass.

[0061] The glycerin fueled explosive composition may contain sufficient glycerin and fuel oil and/or other combustible fuel so that the explosive composition is essentially oxygen-balanced. As glycerin is also a fuel, the amount of a combustible fuel that is used in combination with the glycerin to form a glycerin fueled explosive composition may be adjusted accordingly such that the glycerin fueled explosive composition has the desired amount of fuel per unit of oxidizer. To achieve a desirable oxygen balance, glycerin may be present in an amount of from at least about 1 wt % to at least about 15 wt %. The additional combustible fuel (e.g., fuel oil) may be present in an amount from about 1 to 12 wt % based on the weight of the explosive composition.

[0062] Nitrate salt oxidizers may be used as the solid inorganic oxidizers in the glycerin fueled explosive compositions. Nitrate salt oxidizers include, but are not limited to, ammonium nitrate, sodium nitrate, calcium nitrate, magnesium nitrate, hydrazine nitrate, guanidine nitrate, potassium nitrate, or mixtures or combinations thereof.

[0063] Perchlorate salt oxidizers may also be used as the solid inorganic oxidizers in the glycerin fueled explosive compositions. Perchlorate salt oxidizers include, but are not limited to, ammonium perchlorate, sodium perchlorate, calcium perchlorate, urea perchlorate, or guanidine perchlorate, or mixtures or combinations thereof.

[0064] Ammonium nitrate (AN) may be used as the nitrate salt oxidizer in the glycerin fueled explosive composition. Ammonium nitrate may be combined with at least glycerin and fuel oil to produce a “glycerin fueled ANFO” composition. Ammonium nitrate may be present in the explosive in amounts from about 50% to 98% by explosive weight. According to an embodiment, ammonium nitrate is used as the sole solid inorganic oxidizer or it may be used in combination with other nitrates, perchlorates, or other inorganic oxidizers. In another embodiment, up to about 50% of the ammonium nitrate may be replaced with other nitrate salt oxidizers, perchlorate salt oxidizers, and/or other solid inorganic oxidizers, or combinations thereof.

[0065] Particulate ammonium nitrates suitable for use in ANFO blasting explosives are known in the art and any such particulate forms may be used. Factors that affect the oil adsorption of particulate ammonium nitrate include the porosity of the ammonium nitrate, the coating, if any, on the surface of the ammonium nitrate particle, and the surface area of the ammonium nitrate particle. As porosity and surface area of ammonium nitrate particles decrease, the absorbability of the particles decreases. Further, certain coatings tend to decrease the absorbability of the ammonium nitrate particles. Suitable ammonium nitrate particles may be in the form of separate discrete particles such as prills, granules, crystals, pellets, and fines. The ammonium nitrate particles may be of high density (e.g., 0.86-1.1 g/cc or higher), which are of a low porosity (e.g., absorbs less than about 6% oil) or low density (e.g., 0.6-0.85 g/cc), which are of a higher porosity (e.g., absorbs about 6% or more of oil).

[0066] Various additives that are conventionally used in the art may be incorporated into the glycerin fueled explosive compositions to improve sensitivity, density, flowability, stability, and energy. For example, energy increasers such as aluminum, magnesium, aluminum-magnesium alloys, ferrophosphorus, ferrosilicon, lead and its salts and trinitrotoluene may be added. Suitable sensitizers include glass microspheres and other standard air entraining agents.

[0067] To render the glycerin fueled explosive compositions water-resistant, thickeners, cross-linking thickeners, and cross-linking agents may be added to the mixture. These additives may be separately added to the glycerin to accomplish the same purpose. Commonly used thickeners are cold water swellable and able to produce high viscosities within a matter of hours, and included, but are not limited to, guar gums, gum arabic, starches, xanthan gums, polyacrylamide, cellulose and cellulose derivatives. Water blocking agents such as guar gum may be applied as a coating to the ammonium nitrate as taught in U.S. Pat. No. 4,889,570, incorporated herein by reference in its entirety.

[0068] Commercially available cross-linking or non-cross-linking guar gums may be used in the amount of from about 0.2% to 1.5%. Alternatively, a non-cross-linking guar gum may be used and cross-linking can be accomplished with the addition to the glycerin or explosive mixture of about 1.0-1.5% non-cross-linking guar gum based on guar gum concentration. Cross-linkers include antimonates such as potassium antimony tartrate; dichromates; borates such as sodium tetraborate; tannic acids; and other selected organic acids, among others.

[0069] The glycerin fueled explosive compositions may also be made water resistant by coating the explosive composition with a water-in-oil emulsion. Such emulsions are disclosed by Bellairs et al. in U.S. Patent Application Publication No. 2004/0231769 and Waldock et al. U.S. Patent Application Publication No. 2004/0144456, both of which are incorporated herein by reference in their entireties.

[0070] Other additives to the glycerin and/or explosive mixture may include weak acids for pH adjustment. For example, when using gum thickeners with or without cross-linkers, adjustment of the glycerin and/or explosive mixture with glacial acetic acid to a final pH of 5.5-6.5 provides for successful completion of chemical reactions.

[0071] Another feature of an embodiment includes a method of making the inventive glycerin fueled explosive composition. For example, without limitation, the glycerin fueled explosive compositions may be made by any continuous, semi-continuous, or batch process, including those currently used to make ANFO explosive compositions. According to an embodiment, the explosive compositions of the embodiment are formulated by combining the solid inorganic oxidizer(s), e.g., ammonium nitrate particles, and glycerin together and mixing them until the ammonium nitrate particles are coated with the glycerin. In an embodiment, the glycerin used to make the explosive composition is derived from a biomass fuel source. In another embodiment, the glycerin used to make the explosive composition is crude glycerin. In a further embodiment, the method of formulating the explosive composition combines substantially pure glycerin derived from a biomass fuel source or derived from crude glycerin obtained by a process such as transesterification or saponification with the solid inorganic oxidizer(s). In another embodiment the glycerin use in the method of making the explosive composition is pure glycerin, which is derived from a biomass fuel source or other process which produces crude glycerin as a byproduct, wherein the crude glycerin is further modified by neutralization and/or distillation to obtain the substantially pure glycerin or pure glycerin.

[0072] For an explosive composition comprising a mixture of a glycerin, at least one other combustible fuel, and at least one solid inorganic oxidizer (e.g., ammonium nitrate), the above ingredients may be combined and mixed simultaneously or sequentially in any order. For example, fuel oil may be mixed with the glycerin until the components are evenly distributed and mixed. Any carbonaceous material may be used as a non-glycerin fuel in combination with the glycerin and the least one solid inorganic oxidizer. A fuel oil/glycerin mixture is then combined and mixed with the solid inorganic oxidizer(s), e.g., ammonium nitrate particles to distribute the fuel oil/glycerin mixture over the surface of the particles. In the alternative, the glycerin, combustible fuel, and the solid inorganic oxidizer(s), e.g., ammonium nitrate particles, may be combined simultaneously and mixed until a uniform mixture is obtained. Additionally, any of the above optional additives that are to be incorporated into the composition may be added simultaneously with, or subsequent to, the combustible fuel/glycerin/the solid inorganic oxidizer(s), e.g., ammonium nitrate, mixture.

[0073] The mix density of the glycerin fueled explosive composition may be measured as poured bulk density and as tamped bulk density. The poured bulk density of the glycerin fueled explosive composition may be from about 0.6 to about 1.40 g/cc. The tamped bulk density of the glycerin fueled explosive composition may be from about 0.6 to about 1.40 g/cc.

[0074] The glycerin fueled explosive composition may be prepared on site, delivered to on site with a mobile platform, such as on a bulk truck, or may be packaged in a suitable container (e.g., a polyethylene bag).

[0075] According to an embodiment, the glycerin fueled explosive composition may be formulated as a packaged ANFO type blasting agent product. A packaged glycerin fueled ANFO type blasting agent product may be made by mixing a glycerin with AN fines or crushed AN particles (e.g., prills), in order to help reduce the segregation of glycerin from the mixture. Additionally, a gelling agent or other thickening additive may be added to the glycerin or the mixture to help reduce the amount of segregation. After the mixture is prepared, the explosive may be loaded into a borehole. The mixture may then be packaged into a "kraft" paper bag (e.g., having a wax lining), a polyethylene bag, or other suitable (e.g., water resistant) container and stored for future use.

[0076] Another feature of an embodiment includes a method of using the glycerin fueled explosive composition. The glycerin fueled explosive composition may be used according to any known method of using explosive compositions. Generally, the glycerin fueled explosive composition is inserted into a blast hole and detonated. For example, in order to create a tunnel through rock, a number of holes may be drilled into the rock. These holes are referred to as blast holes, which are then filled with explosive. The positions and depths of the blast holes (and amount of explosive each blast hole receives) are determined by a carefully constructed pattern, which, together with the correct timing of the individual explosions, will guarantee that the tunnel will have the desired cross-section. Detonating the explosive will cause the rock to collapse and thus lengthen the tunnel.

[0077] The following examples are illustrative, but not limiting, of the methods and compositions of the present invention. Other suitable modifications and adaptations as would be known to those skilled in the art, based upon the guidance provided herein, are within the spirit and scope of the embodiments.

EXAMPLE 1

Glycerin Material as a Fuel in an ANFO Dry-Mix Type Blasting Agent Product

[0078] A 5 gallon sample of crude Glycerin material was obtained from Smithfield Bioenergy of Cleburne, Tex. The Glycerin sample proved to be a viscous amber liquid, which had a density of 1.25 g/cc at 22° C., and a pH of >11. The tests involved mixing various levels of Glycerin and/or Glycerin/#2 fuel oil with low-density ammonium nitrate prills, to produce an ANFO type blasting agent product.

[0079] As expected, the glycerin sample proved to be readily miscible with water and only partially miscible with diesel fuel oil. A viscosity of 300 cps was measured at 22° C. using a Brooksfield LV viscometer equipped with a #1 spindle and running at a speed of 12 rpm. An oxygen balance value of −121.6 grams O_2/100 grams was calculated for glycerin using a chemical formula of $CH_2OHCHOHCH_2OH$ for glycerin. This oxygen balance value indicated that about an 86/14 ratio of ammonium nitrate to glycerin produces a desirable oxygen balanced explosive mixture.

[0080] A series of screening tests with the glycerin sample were conducted to determine the suitability of the glycerin sample as a fuel ingredient in an ANFO type Blasting Agent product. In these tests, the glycerin was first neutralized to a pH of approximately 5 with a suitable acid (selected from but not limited to citric, sulfuric, hydrochloric, acetic, tartaric or ascorbic acid), and was then mixed with a sample of a mixture of low-density ammonium nitrate (AN) prills (EDC's low density Industrial Grade AN prills) and high density Ag Grade prills (oil absorption/oil adsorption test=4.8% oil, available porosity test=2.7% oil). A mix of 90 parts AN prills, 3 parts #2 fuel oil and 7 parts glycerin was made and loaded into a 6 inch diameter PVC pipe. The mix was quickly shot (within ~4 hours) in order to reduce the degree of segregation. Because of its lower fuel value, a 14% level of Glycerin was chosen to oxygen balance AN, and a 7% Glycerin/3% fuel oil mixture was chosen to oxygen balance AN. For comparative purposes, a standard ANFO mix was also made using the same raw materials (94 parts AN prills/6 parts #2 fuel oil—also very wet mix). The results of these screening tests are given in Table I.

TABLE I

Mix Parameters for Glycerin ANFO Screening Mixes

Ingredients	Mix 02-1 ANFO Standard	Mix 02-2 7 Glycerin/3 FO ANFO Hybrid
Ammonium Nitrate Prills	94.0%	90.0%
#2 Diesel Fuel Oil	6.0%	3.0%
Glycerin	—	7.0%
Mix Consistency	Wet mix but no pooling of liquids.	Wet mix with some pooling of liquids.
*Mix Density	0.95 g/cc	1.05 g/cc

*Relatively high densities as a result of relatively high density of AN prills.

EXAMPLE 2

Unconfined VOD Test

[0081] The two ANFO mixes from Example 1 were hand loaded into 6-inch diameter by 36-inch long PVC pipes (pipes sealed to prevent water penetration). The charges were primed with a one-pound cast booster and shot at a temperature in the 70-75° F. range. Point-to-point VOD probes were attached to the last 6 inch section of each charge. The VOD values are reported in feet/second+/−500 f/s.

TABLE II

Results of Unconfined VOD Test For Glycerin ANFO

Charge	Mix 02-1 ANFO Standard	Mix 02-2 7 Glycerin/3 FO ANFO Hybrid
Six Inch Diameter PVC Pipe	VOD = 11,710 f/s	VOD = 10,420 f/s

[0082] As can be seen, the Glycerin/#2 fuel oil ANFO product proved to be sensitive enough to detonate in the 6 inch diameter unconfined charge, producing a VOD of about 10,420 f/s.

EXAMPLE 3

Glycerin Material as a Fuel in an ANFO Dry-Mix Type Blasting Agent Product

[0083] The screening test of Example 1 was repeated using low density ammonium nitrate prills. These tests involved mixing various levels of Glycerin and/or Glycerin/#2 fuel oil with low-density ammonium nitrate prills (DYNO's low density AN prills from LOMO plant), to produce an ANFO type Blasting Agent product.

[0084] Various ANFO and neutralized crude Glycerin/ANFO mixes were made in a small concrete mixer, and hand loaded into 6-inch diameter schedule 40 steel pipes for VOD and energy tests. The test mixes included an ANFO standard (94 parts AN prills/6 parts #2 fuel oil), a hybrid glycerin/fuel oil ANFO (90 parts AN prills/3 parts #2 fuel oil/7 parts Glycerin), an all-Glycerin ANFO (85 parts AN prills/15 parts Glycerin), and a sand ANFO blank (90 parts AN prills, 3 parts #2 fuel oil/7 parts sand). The mix descriptions and particulars for these ANFO mixes are given in Table III.

TABLE III

Mix Parameters for Glycerin ANFO Screening Mixes

Ingredients	Mix 09-1 ANFO Standard	Mix 09-4 3% FO/7% Sand ANFO Blank***	Mix 13-1 7% Glycerin/3% FO ANFO Hybrid**	Mix 13-2 15% Glycerin ANFO**
DYNO Ammonium Nitrate Prills*	94.0%	90.0%	90.0%	85.0%
#2 Diesel Fuel Oil	6.0%	3.0%	3.0%	—
Glycerin	—	—	7.0%	15.0%
Sand	—	7.0%	—	—
Mix Consistency	Dry mix	Dry mix. Sand tended to segregate during mixing.	Wet mix.	Wet mix.
Mix Density:				
Poured	0.85 g/cc	0.84 g/cc	0.95 g/cc	1.04 g/cc
Tamped	0.92 g/cc	0.90 g/cc	0.96 g/cc	1.04 g/cc

*The AN prills had relatively good porosity. Poured bulk density = 0.82 g/cc. Tamped bulk density = 0.87 g/cc.

**Because of the wet nature of these two mixes, they were made, loaded into the steel pipe containers and detonated as soon as possible.

***Because of the high density of the sand particles, it was somewhat difficult to obtain a completely uniform mixture during the production of this product.

[0085] The ANFO standard proved to be a relatively dry mix, perhaps due to the high porosity of the AN prills used in these tests. Also, the hybrid Glycerin/fuel oil ANFO mix proved to be very wet, however, there was relatively little pooling of the liquid fuels in the bottom of the mixer when mixing was stopped. The all-Glycerin ANFO mix product had a wet appearance. For this reason, the Glycerin containing ANFO mixes were made and shot the same day, generally within a 4 hour period. A gelling agent or other thickening additive may be added to the all-Glycerin ANFO mix product to help reduce the wet appearance.

EXAMPLE 4

Unconfined VOD Test

[0086] VOD tests were conducted using a continuous VOD test method, with the resistance wire VOD probe inserted directly into the powder column. These tests were conducted on the ANFO compositions of Example 3, which had been packaged in 6-inch diameter by 40 inch long steel pipes. The charges were primed with a one-pound cast booster, and detonated under water at a temperature in the 70-75° F. range. A continuous VOD probe was inserted in each charge, with the probe's start end positioned next to the charge's booster.

[0087] The overall VOD value is the average value measured over the entire 36-inch length of the charge. The initial VOD value is the average value measured over the first 18-inch section of the charge, just after the booster. The final VOD value is the average value measured over the last 18-inch section of the charge. The VOD data are summarized in Table IV.

TABLE IV

Results of Unconfined VOD Test For Glycerin ANFO

Product	Initial VOD	Overall VOD	Final VOD
Mix 09-1 ANFO Standard	12,110 f/s	14,530 f/s	14,970 f/s
Mix 09-4 Sand ANFO Blank	11,290 f/s	12,170 f/s	12,860 f/s
Mix 13-1 7% Glycerin/3% FO ANFO Hybrid	13,860 f/s	14,610 f/s	14,760 f/s
Mix 13-2 15% Glycerin ANFO	13,270 f/s	13,660 f/s	13,600 f/s

EXAMPLE 5

Underwater Energy Data Conducted Using the Bjarnholt Test Method

[0088] The ANFO compositions of Example 3 were tested for energy in 6-inch diameter by 18-inch long schedule 40 steel pipe charges, at a temperature in the 70°-75° F. range. The charges had an average explosive weight in the 7.2 to 9.0 kilograms range. The charges were primed with a Trojan 16LP one-pound cast booster. The Bjarnholt test method was used with a charge-to-gauge distance of 5.4 meters and a charge depth of 4.4 meters. DYNO Spartan 450 one-pound cast boosters were used as a calibration standard.

[0089] The Shock Loss Factor (SLF) is related to the explosive's detonation pressure, which is calculated by multiplying a constant by the density and the detonation velocity squared. The SLF is used to correct for the loss in energy as the pressure wave expands outward from the detonating charge to the gauge. The VOD values were measured on the ANFO products packaged in the 6-inch diameter steel pipe charges, with the average VOD being measured over the initial 18-inch section of the charge (next to booster).

TABLE V

Parameters for the Calculation of Shock Loss Factor

Product	Density (Kg/m3)	VOD (m/s)	D.P. (Kbars)	SLF
ANFO Standard Mix 09-1	920	3,692	31.4	1.34
Sand ANFO Blank Mix 09-4	900	3,442	26.1	1.30
7% Glycerin/3% FO ANFO Hybrid Mix 13-1	950	4,226	42.4	1.43
15% Glycerin ANFO Mix 13-2	1040	4,046	42.6	1.43
DYNO Spartan 450	1590	7,284	210.9	2.11

TABLE VI

Average Underwater Shock and Bubble Energy Data (unit weight basis)

Product	Shock Energy	Corrected Shock Energy	Bubble Energy	Total Available Work Energy
ANFO Standard Mix 09-1	312	418	435	853
Sand ANFO Blank Mix 09-4	216	281	334	615
7% Glycerin/3% FO ANFO Hybrid Mix 13-1	298	426	413	839
15% Glycerin ANFO Mix 13-2	239	342	369	711
DYNO Spartan 450	249	525	488	1013

Note:
All the above energy values are expressed in cal/gm. The Specific Shock Energy is the Shock Energy measured at the gauge. The Corrected Shock Energy is calculated by multiplying the Specific Shock Energy by the SLF. The Total Available Work Energy is the sum of the Corrected Shock Energy and the Bubble Energy.

[0090] The average underwater shock and bubble energy values were calculated by taking the corresponding measured energy values, as listed in Table VI, and multiplying these unit weight energy values by the measured product density values of the ANFO compositions. This was done to express the measured energy values on an energy per unit volume basis.

TABLE VII

Average Underwater Shock and Bubble Energy Data (unit volume basis)

Product	Corrected Shock Energy	Bubble Energy	Total Available Work Energy
ANFO Standard Mix 09-1	385	400	785
Sand ANFO Blank Mix 09-4	253	301	554
7% Glycerin/3% FO ANFO Hybrid Mix 13-1	405	392	797
15% Glycerin ANFO Mix 13-2	356	384	740

Note:
All the above energy values are expressed in cal/cc.

[0091] Table VII shows that the Glycerin/fuel oil hybrid ANFO product appeared to produce more Shock energy, while the standard ANFO product appeared to produce more Bubble energy.

EXAMPLE 6

Modified ANFO Test Batches

[0092] GX Superfuel by-product was evaluated to determine its usefulness as a fuel ingredient in an ANFO type Blasting Agent explosive product. These tests were conducted with a sample of GX Superfuel by-product taken directly off the biodiesel production line at the Smithfield Bioenergy plant at Cleburne, Tex. An analysis of the GX Superfuel showed it to have a pH in the 12.0-13.0 range and to contain crude glycerin with a methanol content of approximately 30% methanol. The GX Superfuel sample was neutralized with acetic acid to a pH of 6.0, and tested for use as a fuel ingredient (mixed 50/50 with other organic fuels) in ANFO type Blasting Agent products. Additional ANFO type Blasting Agent products were made using the GX Superfuel, which had been distilled to lower the methanol to less than 1%. The methanol was then replaced with either isopropyl alcohol or ethanol as alternative alcohols.

[0093] The modified ANFO mixes were made in a pilot plant concrete mixer by first adding the #2 fuel oil and the additional fuel (e.g. #2 fuel oil and used motor oil in Mix #1) to the AN prills followed by the GX Superfuel. The ANFO mixes were packaged in 6 inch diameter PVC pipes for unconfined VOD tests. As expected, when taking into account the limited porosity of the ammonium nitrate prills, the 10% fuel level in the ANFO products produced damp mixes. However, the absorption and adsorption capabilities of the AN prills seemed to be adequate enough to avoid any free liquid from running out of the mix and pooling in the bottom of the mixer.

TABLE VIII

Mix Parameters for Modified ANFO Test Batches

Mix Description	Ingredients	Percentage	Weight (lbs)
Mix #1: GX Superfuel and FO/waste motor oil ANFO	DYNO Low Density Ammonium Nitrate Prills*	90.0%	36.0
	GX Superfuel**	7.0%	2.8
	Waste Motor Oil	1.5%	0.6
	#2 Fuel Oil	1.5%	0.6
Tamped density = 0.96 g/cc. Produced a damp mix, but no free liquid pooled in mixer.			
Mix #2: 50/50 GX Superfuel/Propylene Glycol and FO ANFO	DYNO Ammonium Nitrate Prills*	90.0%	36.0
	GX Superfuel**	3.5%	1.4
	Propylene Glycol	3.5%	1.4
	#2 Fuel Oil	3.0%	1.2
Tamped density = 0.95 g/cc. Produced a damp mix, but no free liquid pooled in mixer.			
Mix #3: 50/50 GX Superfuel/Diethylene Glycol and FO ANFO	DYNO Ammonium Nitrate Prills*	90.0%	36.0
	GX Superfuel**	3.5%	1.4
	Diethylene Glycol	3.5%	1.4
	#2 Fuel Oil	3.0%	1.2
Tamped density = 0.95 g/cc. Produced a damp mix, but no free liquid pooled in mixer.			
Mix #4: 50/50 GX Superfuel/Ethylene Glycol and FO ANFO	DYNO Ammonium Nitrate Prills*	90.0%	36.0
	GX Superfuel**	3.5%	1.4
	Ethylene Glycol	3.5%	1.4
	#2 Fuel Oil	3.0%	1.2
Tamped density = 0.96 g/cc. Produced a damp mix, but no free liquid pooled in mixer.			
Mix #5: 50/50 GX Superfuel/DOT-3 Brake fluid and FO ANFO	DYNO Ammonium Nitrate Prills*	90.0%	36.0
	GX Superfuel**	3.5%	1.4
	DOT-3 Brake Fluid***	3.5%	1.4
	#2 Fuel Oil	3.0%	1.2
Tamped density = 0.94 g/cc. Produced a damp mix, but no free liquid pooled in mixer.			
Mix #6: 75/25 distilled GX Superfuel/Isopropyl Alcohol and FO ANFO	DYNO Ammonium Nitrate Prills*	90.0%	36.0
	GX Superfuel****	5.25%	2.1
	Isopropyl Alcohol	1.75%	0.7
	#2 Fuel Oil	3.0%	1.2
Tamped density = 0.94 g/cc. Produced a damp mix, but no free liquid pooled in mixer.			
Mix #7: 75/25 GX Superfuel/Ethanol and FO ANFO	DYNO Ammonium Nitrate Prills*	90.0%	36.0
	GX Superfuel****	5.25%	2.1
	Ethanol	1.75%	0.7
	#2 Fuel Oil	3.0%	1.2

Tamped density = 0.94 g/cc. Produced a damp mix, but no free liquid pooled in mixer.

*The DYNO AN prills had relatively good porosity. Poured bulk density = 0.82 g/cc.
Tamped bulk density = 0.87 g/cc.

**The GX Superfuel used in these ANFO mixes had been neutralized to a pH of 6.0 using acetic acid and contained about 30% methanol.

***The DOT-3 brake fluid was a mixture of various glycols (triethylene glycol, polyethylene glycol, pentaethylene glycol, diethylene glycol, tetraethylene glycol, polyalkene glycol plus proprietary additives, according to the manufacturer's MSDS of the product).

****The GX Superfuel used in these ANFO mixes had been neutralized to a pH of 6.0 using acetic acid and then had its methanol content reduced to <1% using a "Roto-Vap" distillation technique.
The distilled GX Superfuel was then mixed with the respective alcohol (isopropyl alcohol or ethanol) at a 75/25 blend ratio.

[0094] VOD tests were conducted on the seven modified ANFO test products, which had been packaged in 6 inch diameter by 40 inch long PVC pipes. The charges were primed with a two pound cast booster, and detonated under water at a temperature in the 65-70° F. range. A continuous VOD probe was inserted in each charge, with the probe's start end positioned next to the charge's booster. FIGS. **4-10** illustrate the VOD traces of Mix #1, Mix #2, Mix #3, Mix #4, Mix #5, Mix #6, Mix #7, respectively.

[0095] The overall VOD value is the average value measured over the entire 36 inch length of the charge (probe). The initial VOD value is the average value measured over the first 18 inch section of the charge, just after the booster. The final VOD value is the average value measured over the last 18 inch section of the charge. The VOD data are summarized in Table IX.

TABLE IX

Unconfined VOD Test Data For Modified ANFO Test Batches

Product	Initial VOD	Overall VOD	Final VOD
Mix #1: GX Superfuel and FO/waste oil ANFO	10,230 f/s	11,410 f/s	12,690 f/s
Mix #2: 50/50 GX Superfuel/Propylene Glycol and FO ANFO	10,300 f/s	11,860 f/s	12,300 f/s
Mix #3: 50/50 GX Superfuel/Diethylene Glycol and FO ANFO	10,990 f/s	12,310 f/s	12,930 f/s
Mix #4: 50/50 GX Superfuel/Ethylene Glycol and FO ANFO	10,610 f/s	12,830 f/s	13,220 f/s
Mix #5: 50/50 GX Superfuel/DOT-3 Brake fluid and FO ANFO	9,970 f/s	12,410	13,380 f/s
Mix #6: 75/25 distilled GX Superfuel/Isopropyl Alcohol and FO ANFO	8,620 f/s	10,550 f/s	12,550 f/s
Mix #7: 75/25 GX Superfuel/Ethanol and FO ANFO	11,110 f/s	12,210 f/s	13,090 f/s

[0096] Although the invention has been described with reference to various embodiments and examples, those skilled in the art recognize that various modifications may be made to the invention without departing from the spirit and scope thereof.

[0097] All of the above U.S. patents, U.S. patent application publications, U.S. patent applications, foreign patents, foreign patent applications and non-patent publications referred to in this specification are incorporated herein by reference, in their entirety.

What is claimed is:

1. An explosive composition comprising a glycerin and at least one oxidizer.

2. The explosive composition of claim **1**, further comprising at least one non-glycerin combustible fuel.

3. The explosive composition of claim **1**, wherein the glycerin is provided in a solution comprising methanol and the glycerin.

4. The explosive composition of claim **3**, wherein the glycerin is derived from a biomass fuel source.

5. The explosive composition of claim **3**, wherein the glycerin is crude glycerin.

6. The explosive composition of claim **3**, wherein the glycerin is substantially pure glycerin.

7. The explosive composition of claim **3**, wherein the glycerin is pure glycerin.

8. The explosive composition of claim **4**, wherein the biomass fuel source is wood and forest residue, animal manure and waste, grains, plants, crops or aquatic plants.

9. The explosive composition of claim **5**, wherein the crude glycerin is modified by being neutralized.

10. The explosive composition of claim **9**, wherein the crude glycerin is modified by distillation before being neutralized, after being neutralized or before and after being neutralized.

11. The explosive composition of claim **1**, wherein the at least one non-glycerin combustible fuel is selected from the group consisting of fuel oil, heating oil, diesel fuel, jet fuel, kerosene, alcohols, ethylene glycol, propylene glycol, polymeric product, waste motor oil, diethylene glycol, brake fluid, isopropyl alcohol, ethanol, cellulosic materials, low density cellulosic materials, coal dust, coal powder and combinations thereof.

12. The explosive composition of claim **1**, wherein the at least one oxidizer is a solid inorganic oxidizer.

13. The explosive composition of claim **12**, wherein the at least one solid inorganic oxidizer is selected from the group consisting of ammonium nitrate, sodium nitrate, potassium nitrate, calcium nitrate, guanidine nitrate, hydrazine nitrate, ammonium perchlorate, sodium perchlorate, calcium perchlorate, guanidine perchlorate, urea, urea nitrate, methylamine nitrate, hexamine nitrate, hexamine, ethylene diamine, ethylene diamine dinitrate, and combinations thereof.

14. The explosive composition of claim **13**, wherein the at least one solid inorganic oxidizer is ammonium nitrate, said ammonium nitrate comprising at least 50% of the solid inorganic oxidizer present in the explosive composition.

15. The explosive composition of claim **1**, wherein the explosive composition has a poured bulk density from about 0.75 to about 1.25 g/cc.

16. The explosive composition of claim **15**, wherein the explosive composition has a poured bulk density from about 0.84 to about 0.95 g/cc.

17. The explosive composition of claim **1**, wherein the explosive composition has an oxygen balance of about +5 to −20.

18. The explosive composition of claim **1**, additionally comprising at least one additive.

19. The explosive composition of claim **18**, wherein the at least one additive is selected from the group consisting of aluminum, magnesium, aluminum-magnesium alloys, ferrophosphorus, ferrosilicon, lead, lead salts, trinitrotoluene, and combinations thereof.

20. The explosive composition of claim **19**, additionally comprising glass microspheres.

21. The explosive composition of claim **18**, wherein the at least one additive is selected from the group consisting of guar gums, gum arabic, starches, xanthan gums, polyacrylamide, cellulose, cellulose derivatives, antimonates, pyroantimonates, potassium antimony tartrate, dichromates, borates, sodium tetraborate, tannic acids, and combinations thereof.

22. An explosive composition comprising a glycerin, ammonium nitrate, and a non-glycerin combustible fuel oil.

23. The explosive composition of claim **22**, wherein the glycerin is derived from a biomass fuel source.

24. The explosive composition of claim **22**, wherein the glycerin is crude glycerin.

25. The explosive composition of claim **22**, wherein the glycerin is substantially pure glycerin.

26. The explosive composition of claim **22**, wherein the glycerin is pure glycerin.

27. The explosive composition of claim **23**, wherein biomass fuel source is wood and forest residue, animal manure and waste, grains, plants, crops or aquatic plants.

28. The explosive composition of claim **24**, wherein the crude glycerin is modified by being neutralized.

29. The explosive composition of claim **28**, wherein the crude glycerin is modified by distillation before being neutralized, after being neutralized or before and after being neutralized.

30. The explosive composition of claim **22**, wherein the glycerin is at least about 5% by weight, and wherein the percent by weight is determined solely on the relative portions of glycerin, ammonium nitrate, and non-glycerin combustible fuel oil.

31. The explosive composition of claim **22**, wherein the ammonium nitrate is 50-94% by weight.

32. The explosive composition of claim **22**, wherein the combustible non-glycerin fuel oil is 1-6% by weight.

33. The explosive composition of claim **22**, wherein the explosive composition has an oxygen balance of about +5 to −20.

34. The explosive composition of claim **22**, additionally comprising a gelling agent or other thickening additive.

35. An explosive composition comprising crude glycerin derived from a biomass fuel source, at least one oxidizer, and at least one non-glycerin combustible fuel.

36. The explosive composition of claim **35**, wherein the biomass fuel source is wood and forest residue, animal manure and waste, grains, plants, crops or aquatic plants.

37. The explosive composition of claim **36**, wherein the crude glycerin is modified.

38. The explosive composition of claim **35**, wherein the at least one non-glycerin combustible fuel is selected from the group consisting of fuel oil, heating oil, diesel fuel, jet fuel, kerosene, alcohols, ethylene glycol, propylene glycol, polymeric product, waste motor oil, diethylene glycol, brake fluid, isopropyl alcohol, ethanol, cellulosic materials, low density cellulosic materials, coal dust, coal powder and combinations thereof.

39. The explosive composition of claim **35**, wherein the at least one oxidizer is a solid inorganic oxidizer.

40. The explosive composition of claim **39**, wherein the at least one solid inorganic oxidizer is selected from the group consisting of ammonium nitrate, sodium nitrate, potassium nitrate, calcium nitrate, guanidine nitrate, hydrazine nitrate, ammonium perchlorate, sodium perchlorate, calcium perchlorate, guanidine perchlorate, urea, urea nitrate, methylamine nitrate, hexamine nitrate, hexamine, ethylene diamine, ethylene diamine dinitrate, and combinations thereof.

41. The explosive composition of claim **39**, wherein the at least one solid inorganic oxidizer is ammonium nitrate, said ammonium nitrate comprising at least 50% of the solid inorganic oxidizer present in the explosive composition.

42. The explosive composition of claim **35**, wherein the explosive composition has a poured bulk density from about 0.75 to about 1.25 g/cc.

43. The explosive composition of claim **42**, wherein the explosive composition has a poured bulk density from about 0.84 to about 0.95 g/cc.

44. The explosive composition of claim **35**, wherein the explosive composition has an oxygen balance of about +5 to −20.

45. The explosive composition of claim **35**, additionally comprising at least one additive.

46. The explosive composition of claim **45**, wherein the at least one additive is selected from the group consisting of aluminum, magnesium, aluminum-magnesium alloys, ferrophosphorus, ferrosilicon, lead, lead salts, trinitrotoluene, and combinations thereof.

47. The explosive composition of claim **46**, additionally comprising glass microspheres.

48. The explosive composition of claim **45**, wherein the at least one additive is selected from the group consisting of guar gums, gum arabic, starches, xanthan gums, polyacrylamide, cellulose, cellulose derivatives, antimonates, pyroantimonates, potassium antimony tartrate, dichromates, borates, sodium tetraborate, tannic acids, and combinations thereof.

49. An explosive composition prepared by a method comprising combining a glycerin, a solid inorganic oxidizer, and a non-glycerin combustible fuel.

50. The explosive composition of claim **49**, wherein the glycerin is derived from a biomass fuel source.

51. The explosive composition of claim **49**, wherein the glycerin is crude glycerin.

52. The explosive composition of claim **50**, wherein biomass fuel source is wood and forest residue, animal manure and waste, grains, plants, crops or aquatic plants.

53. The explosive composition of claim **51**, wherein the crude glycerin is modified.

54. An explosive composition prepared by a method comprising combining crude glycerin derived from a biomass fuel source, a solid inorganic oxidizer, and a non-glycerin combustible fuel.

55. The explosive composition of claim **54**, wherein biomass fuel source is wood and forest residue, animal manure and waste, grains, plants, crops or aquatic plants.

56. The explosive composition of claim **54**, wherein the crude glycerin is modified by being neutralized.

57. The explosive composition of claim **56**, wherein the crude glycerin is modified further by distillation before being neutralized, after being neutralized or before and after being neutralized.

58. A packaged blasting agent comprising an explosive composition, wherein the explosive composition comprises a glycerin, ammonium nitrate, and a non-glycerin combustible fuel oil, and wherein said explosive composition is contained in a water-resistant package or is coated with a water-blocking agent.

59. The packaged blasting agent of claim **58**, wherein explosive composition is coated with a water-blocking agent, said water-blocking agent is a guar gum or a water in oil emulsion.

60. The packaged blasting agent of claim **58**, wherein of the explosive composition has an oxygen balance of about +5 and −20.

61. The packaged blasting agent of claim **58**, wherein the explosive composition additionally comprises a gelling agent or other thickening additive.

62. The packaged blasting agent of claim **58**, wherein the glycerin is derived from a biomass fuel source.

63. The packaged blasting agent of claim **58**, wherein the glycerin is crude glycerin.

64. The explosive composition of claim **63**, wherein the crude glycerin is modified.

65. A packaged blasting agent comprising an explosive composition, wherein the explosive composition comprises crude glycerin derived from a biomass fuel source, ammonium nitrate, and a non-glycerin combustible fuel oil, and wherein said explosive composition is contained in a water-resistant package or is coated with a water-blocking agent.

66. The packaged blasting agent of claim **65**, wherein explosive composition is coated with a water-blocking agent, said water-blocking agent is a guar gum or a water in oil emulsion.

67. The packaged blasting agent of claim **65**, wherein of the explosive composition has an oxygen balance of about +5 and −20.

68. The packaged blasting agent of claim **65**, wherein the explosive composition additionally comprises a gelling agent or other thickening additive.

69. The explosive composition of claim **65**, wherein biomass fuel source is wood and forest residue, animal manure and waste, grains, plants, crops or aquatic plants.

70. The explosive composition of claim **65**, wherein the crude glycerin is modified.

71. A method for preparing an explosive composition comprising combining a glycerin, a solid inorganic oxidizer, and at least one non-glycerin combustible fuel.

72. The method of claim **71**, wherein the solid inorganic oxidizer is ammonium nitrate.

73. The method of claim **72**, wherein the ammonium nitrate is provided in a form selected from the group consisting of prills, granules, crystals, pellets, fines, and combinations thereof.

74. The method of claim **72**, wherein the ammonium nitrate is provided as prills.

75. The method of claim **74**, wherein the ammonium nitrate prills have a density of 0.6-0.85 grams per cubic centimeters.

76. The method of claim **71**, wherein the glycerin is derived from a biomass fuel source.

77. The method of claim **71**, wherein the glycerin is crude glycerin.

78. The method of claim **77**, wherein the crude glycerin is modified.

79. The method of claim **71**, wherein the combining is followed by mixing, wherein the combining and the mixing occur on a mobile platform.

80. A method for preparing an explosive composition comprising combining a crude glycerin derived from a biomass fuel source, ammonium nitrate, and a non-glycerin combustible fuel oil.

81. The method **80**, wherein the crude glycerin is modified.

82. A method of using an explosive composition comprising loading the explosive composition of claim **1** into a blast hole and detonating the explosive composition.

83. The method of claim **82**, wherein the glycerin is derived from a biomass fuel source.

84. The method of claim **82**, wherein the glycerin is crude glycerin.

85. The explosive composition of claim **84**, wherein the crude glycerin is modified.

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