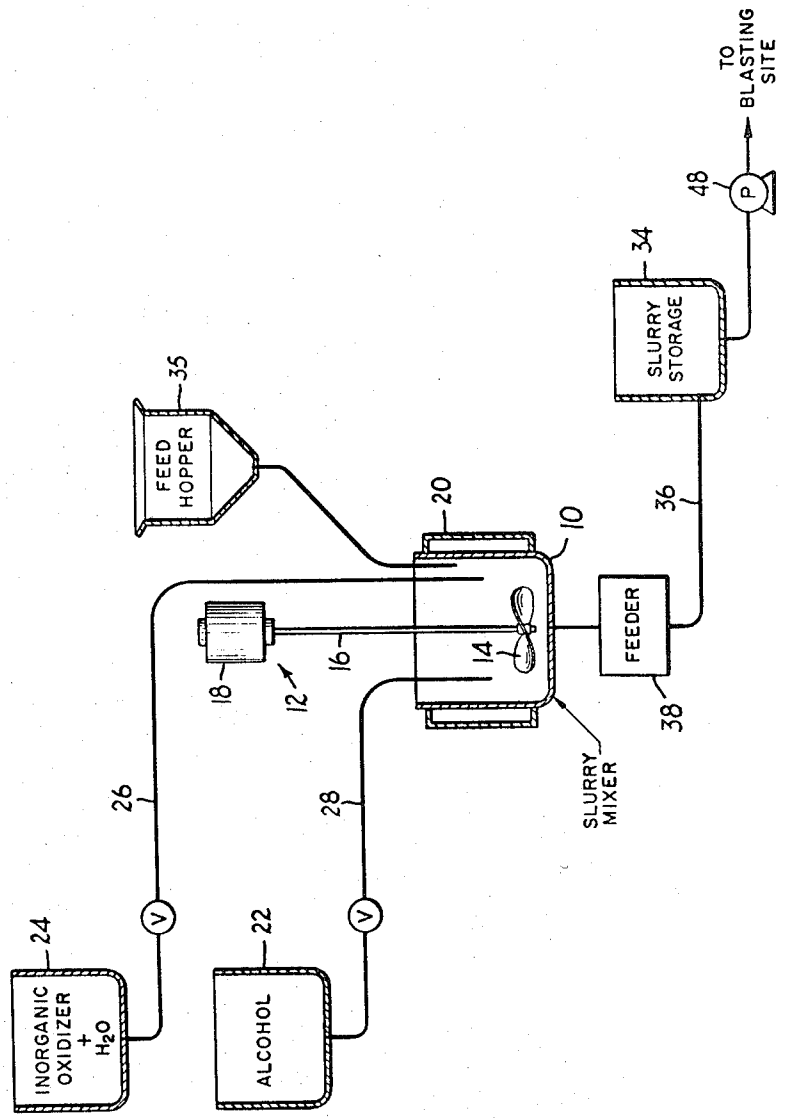
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PROCESS OF BLASTING WITH THICKENED SLURRIED INORGANIC OXIDIZER SALT-ALCOHOL-WATER EXPLOSIVE MIXTURES

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PROCESS OF BLASTING WITH THICKENED SLURRIED INORGANIC OXIDIZER SALT-ALCOHOL-WATER EXPLOSIVE MIXTURES

Jesse B. Bronstein, Jr., Allentown, Pa., assignor, by mesne assignments, to Commercial Solvents Corporation, a corporation of Maryland

Original application Aug. 1, 1966, Ser. No. 569,325, now Patent No. 3,395,056, dated July 30, 1968. Divided and this application Oct. 11, 1967, Ser. No. 681,951

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15 Claims

ABSTRACT OF THE DISCLOSURE

A process of blasting is provided wherein the explosive mixture employed is made in situ proximate to the blasting site, by mixing an inorganic oxidizer salt, a lower aliphatic alcohol fuel in an amount of at least 75% of the amount required to oxygen-balance the oxidizer, and an alcohol thickening agent with sufficient water to slurry the mixture. The thickened slurry is then delivered to the blasting site, confined, such as by depositing the slurry in a bore hole, and detonated.

This application is a division of application S.N. 569,325 filed Aug. 1, 1966 and now U.S. Patent 3,395,056.

This invention relates to a process of blasting wherein thickened explosive slurries comprising an inorganic oxidizer, a lower aliphatic alcohol and, water as the essential ingredients, formed at the blasting site are confined and then detonated, desirably with the aid of a primer.

Explosive muxtures containing relatively large amounts of water have recently become of considerable interest in the explosive art. They have greater versatility than dry mixtures, because they can be used under conditions where water cannot be excluded, and the flowable slurries also may be brought more easily to certain types of sites, such as bore holes and rock crevices. The water content is more than that which is absorbed by the components of the mixture, and is sufficient to act as a suspending agent for the mixture. Such a water content in most cases ranges from about 5% to more than 30%, depending upon the materials present in the mixture and upon the consistency desired.

A slurry having a reasonably stiff consistency containing as little as 5% water may be preferred for use in bulk in wet bore holes, where the composition may be diluted with water already present. Thickening or gelatinizing agents maye be employed when thick slurries are required containing high proportions of water, or when large amounts of water are present in a blast hole. A slurry which can be poured may be desirable for use in bulk in dry bore holes and such a slurry is easily obtained by using a rather large proportion of water, for example 20% or more, without a thickening or gelatinizing agent.

Explosive slurries are described in U.S. Patent No. 2,930,685 to Cook and Farnam, patented Mar. 29, 1960. These compositions are based upon ammonium nitrate, are sensitized wtih TNT, and may contain powdered aluminum. The slurries are asserted to have a high strength, and an ammonium nitrate-fuel oil mixture (94/6 AN-fuel oil) is employed as a standard for evaluation of their strength with the comment that ammonium nitrate-fuel oil mixtures are, of course, not suitable for underwater use unless waterproof.

Ammonium nitrate-fuel oil mixtures have been employed as explosives for blasting purposes for many years, and their effectiveness is well recognized, leading, of course, to the use of such a mixture as a standard for the

Cook et al. evaluation. However, ammonium nitrate and fuel oil alone are not sufficiently sensitive to be detonable by ordinary means, such as blasting caps, and normally are sensitized by the addition of sensitizing explosives such as nitrated toluenes and the like. Alternatively, the dry mixture is poured into a blast hole containing a sensitizing explosive such as TNT to assist in the detonation. Even these mixtures, however, are poor in sensitivity, and occasionally fail to detonate.

U.S. application Ser. No. 855,558 to Towle, now U.S. Patent No. 3,236,180 issued Feb. 22, 1966, describes aqueous inorganic nitrate-fuel oil explosive slurries, which are thickened by the addition of thickening agents such as guar gum, starch, and carboxymethyl cellulose. The fuel oil is of course, water-immiscible and hence might tend to separate out were it not for the fact that only relatively small amounts are used, and the thickness of the slurry also aids in keeping the mixture uniform. However, the oil interferes with the thickening agent, and thickened slurries are hard to obtain.

Fuels other than fuel oil that are more compatible in aqueous slurries would be useful, but the available fuels have presented additional problems. It is more difficult to slurry a solid than a liquid to form a suspension that can be kept a reasonably homogeneous mixture, and most other carbonaceous and metallic fuels are of course solids. Furthermore, in the absence of a sensitizing explosive, detonation becomes more difficult, which limits the types of fuels that can be used to those that form detonable mixtures with inorganic oxidizer.

In accordance with the instant invention, a process of blasting is provided wherein thickened aqueous explosive slurries based on an inorganic oxidizer and employing a water-soluble lower aliphatic alcohol as a fuel, together with an alcohol thickening agent, are formed at the blasting site. Such slurries are simple to prepare, and are readily prepared at the blasting site for immediate use. They can also be prepared in advance, in which case, if the slurry shows a tendency to thin out on storage, the pH of the slurry can be brought to outside of the range from about 4 to about 7, i.e., to below pH 4, and above pH 7, by addition of an acid, an alkali, or an acidic or alkaline buffer.

The thickened aqueous slurried inorganic oxidizer-lower aliphatic alcohol fuel explosive mixtures are detonable in the absence of admixed sensitizing explosives such as trinitrotoluene. Such explosive mixtures are detonated under great confinement, and must be primed with a sufficient amount of highly brisant explosive. However, thickened aqueous slurries including a sensitizing explosive can be employed.

The water serves an important function in the composition. It permits the obtention of a high density which makes it possible to put a large amount of explosive in a given volume in a blast hole. Thus, it is possible to use fewer blast holes for any given operation. It also makes possible a higher rate of detonation, which gives better rock breakage. Also, a higher explosive power may be obtained.

If no sensitizing explosive is present, it is important to use enough of the primer. From about 1 to about 3 pounds, preferably from about 1 to 2 pounds, of primer, referred to herein as the minimum amount of primer, should be used for each unit of length of the mass of explosive. This unit of length varies with the diameter of the mass, and is equal numerically in feet of length to the number of inches in diameter of the mass. This unit of length is hence measured in diameter inch-feet.

For example, in a 5 inch diameter bore hole, one unit of primer is used for each rise of 5 feet or less in the hole. In an 8 inch hole, one unit of primer must be used for each 8 feet or less of rise.

It is also important that a larger amount of primer within the stated range be employed with the smaller diameter masses or columns of explosive, because of the greater difficulty of propagation through the explosive mixture. The ease of propagation increases with increase in diameter of the column of explosive. In 3 and 4 inch diameter columns, a priming unit of less than 2 pounds of primer preferably should not be used, whereas in holes of 8 inches in diameter and greater, the primer may be as little as 1 pound for every 8 feet or less of rise, but under adverse conditions it may be desirable to use somewhat larger amounts.

The primer explosive is used in compacted form, suitable in the form of cast or compressed units.

As the primer any explosive of high brisance can be employed. The higher the rate of detonation, the better. It should have a detonation rate of at least 5000 meters per second, and preferably not below 6000 meters per second. Such explosives are well known to those skilled in this art. Pentolite (an equal parts by weight mixture of pentaerythritol tetranitrate and trinitrotoluene), composition B (up to 60% RDX, up to 40% TNT, 1 to 4% wax), cyclotol (composition B without the wax), tetryl, cyclonite (RDX, cyclotrimethylene trinitroamine), and jentaerythritol tetranitrate are exemplary.

The confinement must be very great. Confinement in ordinary metal, plastic, wooden or cardboard containers is not sufficient, but such containers can, of course, be used for packaging purposes, since the charge detonates when placed under sufficiently high confinement, such as in a quarry blast hole, or under a sufficient head of water. Good detonation is obtained in bore and blast holes in solid rock, such as in a quarry, and such confinement would usually be employed.

The relative proportions of inorganic oxidizer and fuel, i.e., a water soluble alcohol and any supplemental fuels, will depend upon the oxygen balance, and are not critical beyond this. The oxygen balance in turn is dependent upon the particular fuels used and upon the oxidizer. For optimum effect, the fuel is used in an amount sufficient to oxygen balance the oxidizer, but slightly more or less than this can be used, within the range of from about 75 to about 125% of oxygen balance, without disadvantageously affecting efficiency to a serious extent. An amount over 125% of that required to oxygen balance the oxidizer can be used, but would be wasteful because of the loss in efficiency.

The inorganic oxidizer which can be employed in the thickened explosive slurry can be an inorganic nitrate. Ammonium nitrate and nitrates of the alkali and alkaline earth metals, such as sodium nitrate potassium nitrate, calcium nitrate, magnesium nitrate, strontium nitrate and barium nitrate, are exemplary inorganic nitrates. Mixtures of several nitrates such as, for example, mixtures of sodium and ammonium nitrates, also yield excellent results.

As the inorganic oxidizer there can also be used a chlorate or a perchlorate of an alkali or alkaline earth metal, such as sodium chlorate, potassium chlorate, barium chlorate, sodium perchlorate, potassium perchlorate, barium perchlorate, and calcium perchlorate. Mixtures of nitrates, chlorates and perchlorates, of nitrates and chlorates, of nitrates and perchlorates, and of chlorates and perchlorates, can be used.

When mixtures of ammonium oxidizer and the other oxidizer are used, the relative proportion of ammonium oxidizer is important for good explosive shock and power. The ammonium oxidizer is employed in a proportion within the range from about 50 to 95% by weight of the total oxidizer, and the other oxidizer or oxidizers in the proportion of from about 5 to about 50% of the total oxidizer. For optimum power, the proportions are from 80 to 90% ammonium oxidizer, and from 10 to 20% other oxidizer or oxidizers. The proportions of oxidizers selected within these ranges will depend upon the sensitivity and explosive effect desired, and these in turn are dependent upon the particular oxidizer used.

The inorganic oxidizer can be fine, coarse, or a blend of fine and coarse materials. Mill and prill inorganic oxidizers are quite satisfactory. For best results, the inorganic oxidizers should be fine-grained.

The principal fuel employed in the thickened explosive slurry is a water soluble lower aliphatic alcohol having from one to about four carbon atoms, such as methanol, ethanol, n-propanol, isopropanol, isobutanol, butanol-1, butanol-2, and tertiary butyl alcohol.

Methanol is the preferred fuel due to its ability to form explosive mixtures wih inorganic oxidizers that are detonable with high brisance. Methanol supplies 1.5 g. of oxygen balance per gram of methanol.

Aqueous alcohol solutions including an inorganic oxidizer can be thickened to any desired consistency by addition thereto of any known alcohol thickening agent. In this way, it is possible to prepare a thick slurry or even a gel containing a large proportion of water for use in bulk in large blast holes. The thickening agent is water-soluble or water-dispersible. Where desired, an amount of the thickening agent necessary to form a stable thickened slurry at a pH below about 4 and above about 7, can be employed. Such thickening agents and the process of thickening aqueous alcohol solutions are well known, and form no part of the instant invention. Typical thickening agents used are modified guar gums, such as the guar gum ethers, for example, methyl hydroxypropyl guar gum, and polyoxyethylene glycols and glycol ethers, such as "UCAR Resin C–149" and "WSR–301."

The amount of thickening agents is not critical and will depend upon the consistency desired. The consistency can range from a thin free-flowing fluid mixture to a semi-solid or barely flowable consistency. Usually from about 0.1% to about 3% thickening agent and from about 1 to about 10% water is sufficient. The alcohol thickening agent should, of course, be stable at the pH at which a stable thickened slurry or gel is formed in the presence of inorganic oxidizer.

To ensure a pH below 4, there can be added any strong inorganic or organic acid, such as nitric, sulfuric, hydrochloric, phosphoric, trichloroacetic, sulfonic, sulfinic, formic, and acid salts such as urea nitrate, urea chloride, and pyridine hydrochloride. The amount required depends upon the strength of the acid or acid salt.

A pH of above about 7 can be obtained by addition of an alkali such as sodium hydroxide, ammonium hydroxide, potassium hydroxide, sodium triphosphate, sodium monohydrogen phosphate, sodium metaborate, sodium tetraborate pentahydrate, potassium carbonate, sodium acetate, and calcium hydroxide.

As indicated hereinbefore, a sensitizing explosive can also be included, as an optional component.

The preferred sensitizing explosive is nitrostarch, but any sensitizing explosive known to the art can be used, alone or in admixture. Known sensitizing explosives which are useful include, for example, trinitrotoluene, dinitrotoluene, pentaerythritol tetranitrate, trimethylolethane trinitrate, pentolite, cyclonite, nitrocellulose, composition B, cyclotol, tetryl, and smokeless powder such as carbine ball powder.

The relative proportions of inorganic oxidizer and of sensitizing explosive will depend upon the sensitivity and explosive shock wave desired, and these, again, are dependent upon the particular nitrate and sensitizing explosive. The proportions are not critical in any way. For optimum effect, the inorganic oxidizer is used in an amount within the range from about 10 to about 95%, and the sensitizing explosive can be used in an amount within the range from 0 to about 40% by weight of the explosive composition. From about 25 to about 30% sensitizing explosive and from about 50 to about 70% inorganic oxidizer give the best results.

When the amount of sensitizing explosive is in the lower

part of the range, or zero, a large booster is needed. At amounts beyond 40%, the sensitizing effect falls off, and is no longer proportional to the amount of sensitizing explosive added, and therefore amounts beyond 40% are not usually used.

Sensitizing explosives of any particle size can be used. They can, for example, be fine, coarse, or a blend of fine and coarse material. Some materials, such as nitrostarch, are commercially available as very finely-divided powders, and so also is trinitrotoluene. Such available materials are employed to advantage, because in most cases they tend to produce compositions having a greater explosive effect and sensitivity.

In addition to these materials, as has been indicated, the thickened explosive slurry can include an active metal fuel, usually, aluminum and preferably in particulate form, for example aluminum powder, atomized aluminum, granular aluminum, or flake aluminum. Aluminum can be used in the form of alloys such as aluminum-magnesium alloys. Other metal fuels can also be used alone or in conjunction with the aluminum, such as, for example, magnesium, ferrosilicon, beryllium, and lithium, and nonmetal element fuels, such as boron. Where the aqueous slurry contains aluminum as a supplemental fuel and the slurry has a pH of less than about 4, the aluminum should be coated with an acid resistant material such as a silicone resin or polytetrafluoroethylene to keep the aluminum from dissolving in the acidic slurry. The metal fuel will usually comprise from about 0.5% to about 50%, and preferably from 0.5 to 40% of the composition, of which fuel preferably at least 50% is aluminum. The size of the metal particles is not relevant to the stabilization of the slurry.

The alcohol is the principal carbonacous fuel, and no other carbonaceous fuel is necessary, or in some cases, even desirable. However, if desired, minor amounts of a solid carbonaceous fuel can be included, such as powdered coal, petroleum oil, coke dust, charcoal, bagasse, dextrine, starch, wood meal, flour bran, pecan meal, and similar nut shell meals. A solid carbonaceous fuel when present will comprise up to about 30% of the mixture. Mixtures of metal and carbonaceous fuels can be used, if desired.

An antacid, or other stabilizing material, such as zinc oxide, calcium carbonate, aluminum oxide and sodium carbonate, can be added, if desired. Such ingredients will comprise from about 0.3 to about 2% of the thickened mixture.

The explosive mixtures contain enough water and alcohol to act as a suspending medium for the solid ingredients, resulting in a slurry. Some solid fuels and nitrates are capable of absorbing surprisingly large amounts of water and alcohol, so that if a slurry is desired, the amount of these fluids added must be more than the amount that will be absorbed and sufficient to suspend the mixture. Usually, a total of 7% water and alcohol is enough both to meet the density requirement and to barely slurry the mixture, when ammonium nitrate is the only oxidizer, but more than this may be required to make the slurry flowable. As little as 5% may be enough to slurry the mixture in the case of certain oxidizer mixtures.

The practical upper limit on the amount of water is set by excessive desensitization and loss of power, and an amount of water in excess of about 50% by weight of the slurry would not be employed.

The mixture is readily prepared by simple mixing of the ingredients. The solid materials, including the oxidizer and any optional ingredients, such as sensitizing explosive, supplemental solid fuels, etc., would usually be mixed to form a homogeneous blend, and then sufficient water and alcohol plus alcohol thickening agent would be added to bring the mixture to the desired consistency, which can range from a thick but flowable slurry, to a barely pourable mixture, up to a firm gel.

In formulating the finished explosive, the blasting site requirements will of course be taken into acount. Thus, a rather thick slurry can be formulated for use in wet bore holes, in which the water can be expected to considerably dilute the slurry after loading. Alternatively, waterproofing agents can be incorporated in the slurry, so as to resist dilution thereof by water present in the hole. Those skilled in the art will appreciate the variations that will be required to ensure detonation under the required conditions.

Because of the availability and ease of mixing of the components, the slurry of the mixture is especially adapted to be made in situ proximate to the blasting site, by mixing the ingredients, thereby forming an explosive slurry comprising the oxidizer, the alcohol as the fuel in an amount to oxygen balance the mixture, a thickening agent, if desired, and water, which desensitizes the explosive mixture. Thereafter, additional formulating components such as additional fuels, oxidizing agents, explosive sensitizers, and the like can be incorporated in the thickened slurry. The so-formed thickened slurry can then be delivered immediately to the blasting site, poured or inserted into the bore hole, and detonated.

Apparatus which can be employed in carrying out the on-site mixing method described above includes, in combination, a mixing vessel in which the inorganic oxidizer, the alcohol, thckening agent and any supplemental components such as explosive sensitizer, supplemental fuels, etc., are mixed, and pumping equipment and related delivery means for delivering the finished slurry to the blasting site, such as a bore hole, where it is to be detonated. The mixing vessel includes stirring means for assisting in the mixing process, and in the formulation of the finished slurried explosives, together with heating means, if required, and means to mix and deliver the starting materials as well as the finished slurry.

To facilitate use of the equipment by large-scale users, the invention also contemplates equipment adapted for the continuous mixing to form the thickened alcohol slurry, means for continuously delivering the slurry to a separate site at which mixing with additional slurry components can be completed, and means for continuously delivering the resulting formulation to the blasting site.

It will be apparent that in this way the invention combines all of the advantages of on-site mixing of slurried explosives, and in addition has the advantage that no storage of explosive starting material at the blasting site or in the vicinity thereof is required.

The figure shows schematically a preferred embodiment of apparatus which can be used in carrying out the process of the invention, mounted on a mobile vehicle to facilitate movement of the apparatus to any desired blasting site.

The apparatus shown in the figure comprises storage reservoirs **22** and **24** for lower aliphatic alcohol and inorganic oxidizer slurried in water. Lines **26** and **28** lead thence to a mixing tank in communication with a slurry storage tank **34** via conduit **36**. A suitable feeder **38**, such as a vibrator, is attached to conduit **36** for uniformly and controllably delivering the explosive slurry components materials from the mixing tank to the storage tank. A pump **48** is provided for transporting explosive slurry from the slurry storage tank **34** to the bore hole or other blasting site.

In operation, the alcohol and aqueous slurried inorganic oxidizer, with thickener added if desired, are fed from the reservoirs **22** and **24** at a predetermined rate through conduits **26** and **28** respectively into the mixing tank **10**, wherein they are mixed, with additional thickener, if desired, from feed hopper **35**, to form a thickened explosive composition. The explosive composition is fed from the mixing tank **10** into the slurry storage tank **34**. The explosive composition and slurry liquid can be held in the slurry storage tank **34**, if desired, or pumped

at once via pump **48** to the bore hole or other blasting site.

The following examples in the opinion of the inventor represent the best embodiments of this invention.

EXAMPLE 1

An explosive mixture of the following composition was made up:

	Parts by weight
Grained ammonium nitrate	84.30
Methanol	10.00
Water	5.00
UCAR Resin C–149	0.65
NH_4OH	0.05
	100.00

This mixture had a pH of 7.6, and was relatively stiff, but could be pumped into a bore hole. When pumped into an 8 inch diameter bore hole immediately after mixing, with 2 pound composition B primers every 8 feet of rise of explosive, it gave complete detonation, and excellent rock breakage.

EXAMPLE 2

An explosive mixture in the form of a thick flowable slurry was prepared, having the following composition:

	Parts by weight
Grained ammonium nitrate	67.4
Methanol	20.0
Water	2.0
Resin WSR 301	0.6
Urea nitrate	10.0
	100.00

The slurry had a ballistic pendulum value of 10.4. It was poured from a container into an 8 inch blast hole. When exploded with 1 pound pentolite primers every 8 feet of rise, it detonated completely, and produced very good rock breakage.

EXAMPLE 3

An explosive mixture in the form of a heavy thick slurry which would completely fill the volume of a large blast hole was prepared, having the following composition:

	Parts by weight
Grained ammonium nitrate	71.0
Methanol	10.0
Water	11.0
Aluminum granules	7.0
UCAR Resin C–149	1.0
	100.0

This mixture was mixed and immediately pumped into a 6¼ inch diameter blast hole in a limestone quarry. The priming consisted of 1 pound pentolite primers, placed ever 3½ to 6½ feet of rise in the blast hole. A total of 600 pounds of the mixture was then stemmed. Upon detonation, the mixture fired completely, and produced very good rock breakage.

EXAMPLE 4

An explosive mixture was prepared, using the composition of Example 3, but substituting prilled ammonium nitrate for the grained ammonium nitrate. The resulting slurry had a consistency which was somewhat more fluid than that of Example 3. This slurry was used to fill a 6¼ inch diameter blast hole in a limestone quarry in two sections. The bottom section was primed with 1 pound pentolite primers for every 4 feet of rise, and the next section with 2 pound pentolite primers for every 4 feet of rise, and the next section with 2 pound pentolite primers for every 5 feet of rise. A total of 600 pounds of explosive slurry was used. When detonated, the mixture fired completely, and the rock breakage was excellent.

EXAMPLE 5

An explosive mixture was made up having the following composition:

	Parts by weight
Ammonium nitrate (crushed prills)	67.4
Methanol	20.0
Water	2.0
Methyl hydroxypropyl guar gum	0.6
Formic acid	2.0
	92.0

This mixture had a pH of 3.1, and a consistency just short of a flowable slurry, but was readily moldable and retained this consistency when stored in closed containers at normal atmospheric temperatures. When exploded in an 8 inch diameter blast hole with 2 pound pentolite primers for every 8 feet of rise of explosive, it gave complete detonation and excellent rock breakage.

Having regard to the foregoing disclosure, the following is claimed as the inventive and patentable embodiments thereof:

1. A process of blasting, which comprisese mixing proximate to the blasting site an inorganic oxidizer salt, a lower aliphatic alcohol fuel in an amount of at least 75% of the amount required to oxygen-balance the oxidizer, and a thickening agent for the alcohol, adding sufficient water to slurry and thicken the mixture and adjust the consistency of the mixture according to the requirements of the blasting site, confining the mixture in a blast hole, and then detonating the confined mixture.

2. A process of blasting in accordance with claim **1** including the step of adjusting the pH of the slurry, if necessary, to below about 4 or above about 7, depending on the requirements of the blasting site.

3. A process of blasting in accordance with claim **1**, wherein the thickening agent for the alcohol is a polyoxyethylene glycol.

4. A process of blasting in accordance with claim **1**, wherein the thickening agent for the alcohol is a guar gum ether.

5. A process of blasting in accordance with claim **1**, wherein the explosive mixture includes a sensitizing explosive.

6. A process of blasting in accordance with claim **1**, which comprises putting the explosive mixture in a container and then confining the container in a blast hole.

7. A process of blasting in accordance with claim **1** in which the inorganic oxidizer salt of the explosive mixture is at least one inorganic nitrate selected from the group consisting of ammonium nitrate and alkali and alkaline earth metal nitrates.

8. A process of blasting in accordance with claim **1** in which the inorganic oxidizer salt of the explosive mixture is at least one inorganic chlorate selected from the group consisting of alkali and alkaline earth metal chlorates and perchlorates.

9. A process of blasting in accordance with claim **1** in which the amount of alcohol present in the explosive mixture is sufficient to oxygen-balance the oxidizer.

10. A process of blasting in accordance with claim **1** wherein the explosive mixture includes an amount of urea nitrate to ensure that the pH of the thickened slurry is below about 4.

11. A process of blasting in accordance with claim **1** wherein the explosive mixture includes aluminum as an active fuel.

12. A process of blasting in accordance with claim **1** wherein the alcohol is selected from the group consisting of methanol, ethanol, n-propanol, isopropanol, isobutanol, butanol-1, butanol-2, and tertiary butyl alcohol.

13. A process of blasting in accordance with claim 1 wherein the explosive mixture is employed in combination with a primer.

14. A process of blasting in accordance with claim 13 in which the primer is an equal parts by weight mixture of pentaerythritol tetranitrate and trinitrotoluene.

15. A process of blasting in accordance with claim 13 in which the primer is a mixture of up to 60% cyclotrimethylene trinitroamine, up to 40% trinitrotoluene, and 1 to 4% wax.

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CARL D. QUARFORTH, Primary Examiner

S. J. LECHERT, Assistant Examiner

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