Title: MODIFIED BLASTING AGENT

Abstract: The present invention relates generally to an explosive composition comprising an aqueous emulsion of: an oxidizer component, a hydrocarbon fuel component containing an emulsifier, and a bulking agent being a fuel-type waste material in a solid particulate form substantially lacking rough surfaces and sharp edges. Preferably the composition is of an ammonium nitrate based emulsion and a pelleted bulking agent. It also involves a method of providing an explosive composition to a blast site using a conventional mobile processing unit (MPU), being a truck having separate compartments adapted for holding fuel oil, dry ammonium nitrate prill, and ammonium nitrate based emulsion, where a compartment instead holds particulate waste material. It also concerns a method of blasting soft and wet ground, which comprises injecting into one or more blast holes in the soft and wet ground a sufficient quantity of the composition, and then setting off the composition.
MODIFIED BLASTING AGENT

TECHNICAL FIELD

[0001] The present invention relates generally to blasting agents and explosive compositions and to methods of making, using and the delivery of such agents. More particularly, the present invention concerns a multi-component explosive formulation which utilises waste materials which otherwise would have been destined for landfill or high temperature incineration. In particularly, though not exclusively, the present invention relates to the manufacture, use and delivery of blasting agents comprising various forms of ammonium nitrate based emulsion explosives, which have been modified by the incorporation of waste material as a component of the explosive.

BACKGROUND ART

[0002] Once a material has served a purpose or is a by-product of an industrial process, it becomes a waste material. There are generally a number of different ways in which it can be managed for its safe and environmentally sustainable disposal. One way is separation, recycling and eventual re-use. Another way is to manufacture the material from easily biodegradable material; so that when the material is finally disposed of in landfill, it has a shorter lifespan there compared to non-biodegradable materials.

[0003] However, there are some materials which cannot be either recycled or made of biodegradable materials. In this situation, the material is managed by either incinerating it or by burying in landfill where it will degrade only slowly. The disposing of waste material in landfill then constrains the use of this land, for example with some waste material such as plastics taking up to 400 years to decay. The burning of waste material such as plastics often requires high temperatures, so that it is difficult and costly to do. But this process may also release harmful pollutants, often in industrial areas where pollution may already be an issue.
One way to address these issues is to incorporate such difficult to recycle or degrade waste material into an explosive composition. The extreme conditions and high temperatures generated when such an explosive composition detonates achieves the purpose of disposing of the material, in an analogous manner to high temperature incineration, but achieving a useful result, and potentially at lower cost.

This approach has previously shown to be achievable for the addition of particulate rubber with solid ammonium nitrate as disclosed in U.S. Patent No. 5,505,800 (Harries et al). This citation is primarily directed to creating "low shock energy explosives" (LSEE). The rubber can be sourced from shredding used tyres. However, the rubber particulates produced have rough edges, which it has since been found can lead to crystallisation in the explosive mixture when the rubber is mixed with ammonium nitrate based emulsions. Crystallisation can prevent the mixture detonating or it will give a poor result.

Another attempt to use waste material in this manner, involves mixing of energetic waste with different explosive compositions such as AN, ANFO, water gels and emulsions, as disclosed in U.S. Patent No. 5,536,897 (Clark et al). This citation generally concerns using waste material contaminated by rocketry fuel. The waste material is then shredded. The presence of residual rocket fuel in the waste ensures that the waste material contributes to the blasting performance of the final explosive. However, the absence of such fuel material in the waste material can result in the explosive composition not detonating.

The presence of shredded material in an emulsion blend may create material with rough edges and these edges can lead to crystallisation of a product. The crystallisation of a product can result in poor performance of the explosive with reduced water resistance and increased risk of post blast fumes.
Accordingly, it would be useful to provide a solution that avoids or ameliorates any of the disadvantages present in the prior art, or which provides another alternative to prior art approaches.

SUMMARY OF THE INVENTION

According to one aspect of the invention there is provided an explosive composition comprising an aqueous emulsion of: an oxidizer component, a hydrocarbon fuel component containing emulsifier, and fuel-type waste material, as a bulking agent, being in a solid particulate form that substantially lacks rough surfaces and sharp edges sufficiently so as to not promote crystallisation of the emulsion.

Another aspect of the invention involves a method of providing an explosive composition to a blast site having one or more blastholes for receiving the composition, by means of a conventional mobile processing unit (MPU), said unit comprising a truck having separate compartments adapted for holding (a) hydrocarbon fuel component such as fuel oil, (b) the dry oxidiser component such as dry ammonium nitrate prill, and (c) the wet oxidiser component such as ammonium nitrate based emulsion, and the unit having means for mixing two or more of the components from compartments (a), (b) and (c) together and injecting the resulting mixture in a blasthole, characterised in that compartment (b) instead holds the bulking agent in the form of particulate waste material, and where a density reducing agent is added to the mixture from compartments (a), (b) and (c) just prior to it being injected into a blast hole, preferably by an auger on the MPU, and wherein the composition is in accordance with the invention.

Yet another aspect of the invention concerns a method of blasting soft and wet ground, which comprises injecting into one or more blast holes in the soft and wet ground a sufficient quantity of the composition according to the invention, and then setting off the composition.

The oxidizer component of the emulsion is generally an aqueous solution or melt containing an oxygen-releasing salt. Preferably the oxygen-releasing salt is selected from one or more of ammonium nitrate, sodium
nitrate, calcium nitrate, or ammonium perchlorate, and most preferably it is ammonium nitrate.

**BRIEF DESCRIPTION OF DRAWINGS**

[0013] Preferred embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings in which: Figure 1 is a schematic of a truck able to be used for delivering blasting explosives, according to the present invention:

Figures 2a and 2b show photographs (not to scale) of two products (A & B) of waste material pellet components that may be used in the invention; and Figure 2c shows another photograph (not to scale) of product B (Figure 2b) waste pellets showing their smooth appearance that may be used in the invention,

Figure 2d shows a photograph (not to scale) of another product of waste pellets, for use in the invention, and

Figures 3a and 3b, show photographs (not to scale) of comparison waste products that do not form part of the invention, showing the roughness and jagged nature of their surfaces, and the sharp edges and corners present.

**DESCRIPTION OF EMBODIMENTS**

[0014] According to the present invention, there is provided an explosive composition, preferably comprising an ammonium nitrate (AN) type based emulsion and a waste material as a bulking agent. The waste material is in solid particulate form.

[0015] The waste material is fuel-type waste material, generally being waste that can combust at high temperatures in the presence of an oxidiser. Generally this waste may be carboniferous materials, such as waste plastics, rubber, paper, waxes, and the like. Some suitable sources of waste material includes nylon pellets, cardboard, polyethylene, wax, and commingled plastic waste. Preferably the solid particulate form is in the form of pellets or the waste material. Some other suitable sources of waste include readily oxidisable metal, such as aluminium.
Commimgled plastics wastes, including a substantial amount of polyethylene and similar plastics, sourced from plastics from domestic waste collections may be utilised. These are generally finely chopped and ground to a powder, and the powder melted or compressed together, and then extruded to form smooth surfaced waste plastic pellets, with rounded corners and edges. Other materials such as commingled paper and cardboard wastes optionally with a waxy wastes, may be shredded and compressed together to form smooth pellets with rounded edges.

The waste material is in a granular or particulate form, preferably having an average particle size of for 0.5 to 10 mm, and more preferably from around 1 to 4 mm, and most preferably around 2 to 3 mm in size. These pellets may be spherical, cylindrical, cube shaped, as square or rectangular blocks, or irregular in shape, with generally smooth surfaces and rounded edges.

It is also a preferred feature that the granular waste material in particulate form should be of a similar size to the particulate solid AN prill that is in the blasting composition. AN prill is typically between 1 to 4 mm in size, and so using particulate waste material that has a similar size distribution is advantageous. The loading equipment is able to function effectively with the prill particles, and so by using waste particles of a similar size, the equipment will also function efficiently with that.

It is also advantageous that the waste material have a density that is not too low, as very low density additives, such as microballoons or styrene beads are known to be added as sensitising agents. Preferably the waste particles can have a density of around 0.2 to 1.0 g/cm³, and more preferably around 0.4 to 0.7 g/cm³. Ideally the waste material particles themselves should not substantially affect the sensitisation of the blasting emulsion.

As described below in more detail, these waste material particles should have relatively smooth surfaces and a minimum of sharp edges, sufficiently so, that they do not destabilise the emulsion, or do not promote
the crystallisation of the emulsion. The stability of the emulsion can be measured using the Rod Rating test, as described below, and preferably, waste type pellets that provide a Rod Rating test result of 6 or higher when mixed with an AN emulsion are ideal for the invention.

[0021] Figures 2a, 2b, 2c, and 2d, show photographs (not to scale) of samples of some pellets that may be used in the present invention. The sample in Figure 2a is sourced from paper and cardboard. The samples in Figures 2b, 2c and 2d, show samples sourced from waste plastics. In these samples, waste high density polyethylene is the major constituent. These samples show smooth outer surfaces and rounded edges and corners. In contrast the samples shown in the photographs for Figures 3a, and 3b show prior art bulking agents, which have rough surfaces, with sharp edges and corners, as well as small sharp whiskers, that destroy the emulsion, if these were to be used in an analogous blasting composition.

[0022] The waste material has the advantage of being unwanted, and also will often be a cost effective material to use as a consequence. Its use also permits the waste to be removed from the environment, by being incinerated in the explosion. Alternatively, fresh plastics material may be used as the source of some (or all), of the fuel type waste material. The term "waste material" is to interpreted broadly in this invention, and while it is preferred to use plastics waste, recycled from other applications, the use of fresh material is also permitted, if it fulfils the same purposes. It is intended that recycled waste would be the primary source, due to its low cost, but at times, there may be shortages of such material, or temporary price rises, or unexpected increase in demand for the blasting composition, and in these circumstances some fresh material may be substituted for the waste.

[0023] In addition, other difficult or expensive to dispose of materials may be included in the waste, especially those that may be expensive to dispose of apart from in a high temperature incinerator, which may be expensive to do. Waste disposal companies may pay to have these components added to the explosive by incorporation in the waste particulate material, thereby improving the economic benefit of producing the blasting
agent of the invention. Any such materials should be included if they will not damage the environment if small quantities do not get completely incinerated. This option is also advantageous if the blasting is of coal, for example that is to be burnt to produce electricity, so that any such materials will then be burnt in any case. Such materials are ideally carboniferous waste products that would otherwise be incinerated, but which can instead be included in the blasting composition. Colourants, such as waste organic dyes and similar materials may be examples of such materials.

[0024] The oxidizer component used in the invention is preferably an ammonium nitrate (AN) based emulsion. However, other oxidizers may be used in place of, or in addition to, ammonium nitrate. These may include alkaline earth nitrates such as calcium nitrate, or alkali metal nitrates such as sodium nitrate, and urea. Some other example may include alkaline earth or alkali metal perchlorates such as for instance, ammonium perchlorate, although these are not often used due to environmental concerns. Most preferably, an aqueous solution of ammonium nitrate is used alone as the oxidizer.

[0025] The hydrocarbon fuel component of the invention is generally fuel oil, such as mineral or diesel oil, as used with conventional ANFO blasting explosives in the quarrying, mining, and civil construction industries.

[0026] The hydrocarbon fuel component contains emulsifier that is a generally any of the emulsifiers used with AN emulsion blasting explosives. A single emulsifier or a combination of emulsifiers may be used. Some preferred emulsifiers may be selected from the group of emulsifiers that result from condensation reactions between PIBSA and amines or alkanolamines. Another example of a suitable emulsifying agent is sorbitan mono-oleate, or the like. A prefererred emulsifier may be selected from of at least one derivative of poly(isobutylene) succinic anhydride or poly(isobutylene) succinic acid emulsifier with diethylethanolamine or other alkanolamines. The emulsifying agent preferably constitutes between 0.3 to 3.5% by weight of the total composition and most preferably from 0.5 to 1.5% by weight.
[0027] Most preferably the waste material used is such that, when mixed with the other AN emulsion components, it does not sensitise the emulsion so as to permit an explosion. This operates as a safety feature to prevent accidental triggering of an uncontrolled explosion.

[0028] Ideally, the mixture of the AN emulsion and the waste material is then sensitised, preferably at the time it is injected into a blast hole, by the addition of a separate sensitisation component. This sensitisation component may be a density reducing agent. One preferred example of a suitable such sensitisation agent is an alkali metal nitrite, and an acid, which when mixed together produce nitrogen gas, thereby reducing the density of the explosive blasting emulsion. Ideally, the density of the emulsion is reduced to less than 1.15 g/cm³ and preferably between 0.80 g/cm³ and 1.15 g/cm³, by selecting a suitable quantity of sensitisation agent to mix with the emulsion.

[0029] The particulate waste material is in solid particulate form, which has particles that substantially lack rough surfaces and sharp edges. This feature will therefore not promote the emulsion crystallising. The absence of sharp/rough edges does not provide a means for disruption, and therefore crystallisation, of the emulsion droplets.

[0030] An amount of simple testing may be carried out to test if any potentially suitable waste particulate will work in the invention. Ideally any waste product may be utilised if it is able to be oxidised in the resulting explosion, and will not destabilise the emulsion. Preferably also, the waste product should not provide sensitisation to the product, to allow the blasting agent to be sensitised separately, at the time it is pumped into the shot holes, by gassing the emulsion to reduce its density, for example.

[0031] Preferably, the waste particulates are in the form of pellets, ideally pellets having rounded and smooth surfaces and edges. These pellets may have an average particle size that is similar to that of AN prill, for example ideally being around 2 to 3 mm in diameter.

[0032] Preferably, the waste matter comprises from 1% to 50% by weight of the total composition, when all the components are combined, prior
to triggering an explosion. More preferably, the waste material comprises from 10% to 40% of the composition.

[0033] The blasting agents of the invention are particularly useful in wet soft ground. Generally an explosive composition has good water resistance if there is 60% or greater emulsion content in the explosive. Therefore, the explosive composition of this invention would generally be good for use in wet ground.

[0034] Soft ground requires less energy for the ground to move. The calculated energy of ANFO is 3.7 MJ/kg compared to one of the formulations for the invention being 2.0 MJ/kg. The relative weight strength of that formulation is 0.54 compared to ANFO of 1.0 and the relative bulk strength at a density of 1.05 g/cc is 0.69 compared to 1.0 for ANFO. Therefore the energy of this product is less than ANFO or even emulsion-ANFO blends and so is better suited for soft ground.

[0035] Preferably the compositions of the invention are delivered to the site where the blasting is to take place using a conventional mobile processing unit (MPU) truck, which is carrying the components in the sections normally used to hold the components of traditional AN emulsion blasting agents. The waste material is stored in and sourced from the storage container usually reserved for the ammonium nitrate used in dry addition, i.e. section (b). The explosive composition is delivered from an auger of the MPU. The density reducing agent is ideally added to the explosive composition before the explosive composition exits from the auger into the blast holes.

EXAMPLES

[0036] Laboratory batches of the ammonium nitrate based emulsion were manufactured as outlined below. Table 1 lists the ingredients and weights used to manufacture the emulsion. Other formulations also fall within the present invention.

[0037] GENERAL EMULSION MANUFACTURE PROCEDURE
The ingredients of the oxidizer phase were heated to 75°C to form an aqueous solution. Separately, the ingredients of the fuel phase were mixed while heating to 65°C. The hot oxidizer phase was then poured into the fuel phase slowly, with agitation provided by a "Lightnin' Labmaster™" mixer fitted with a 65 mm "Jiffy™" stirring blade rotating initially at 600 rpm for 30 seconds. The crude emulsion was refined by stirring at 1000 rpm for 30 seconds, 1400 rpm for 30 seconds and 1700 rpm until the stated viscosity was achieved. The quantity of product prepared in each sample was 2.0 kg.

[0038] This represents a standard formulation that was used as the emulsion source for the different blends. The formulation is shown in Table 1 below.

[0039] The emulsifier was selected from the group of emulsifiers that result from condensation reactions between PIBSA and amines or alkanolamines. The mineral oil used was predominantly paraffinic with some aromatic and naphthenic constituent compounds. The emulsion was formed with a viscosity about 25,000 cP.

[0040] Table 1 - Standard Emulsion Formulation

<table>
<thead>
<tr>
<th>Oxidiser Component</th>
<th>94%</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Ammonium Nitrate</td>
<td>75%</td>
</tr>
<tr>
<td>- Water</td>
<td>25%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hydrocarbon Fuel Component</th>
<th>6%</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Emulsifier</td>
<td>15%</td>
</tr>
<tr>
<td>- Mineral Oil/ Fuel Oil</td>
<td>85%</td>
</tr>
</tbody>
</table>

TABLE 1.

[0041] The waste material was supplied by "Australian Composite Technology" company ("Plasmar") of Victoria Australia. In these examples, the material was supplied in two versions, either in a shredded form or as a pellet.
The material that was shredded generally had sharp edges and this resulted in the destabilisation of the ammonium nitrate based emulsion due to the sharp edges interacting with the droplets in the emulsion and causing crystallisation. The other form, pelletised material, generally did not destabilise the emulsion, although this was also dependent on the material used.

[0042] Four materials were tested, these included (1) nylon pellets, (2) cardboard pellets, (3) pellets which consist of a mixture of cardboard, polyethylene and wax, (called "Product A") and (4) pellets which consist of comingled plastics (called "Product B"). A photograph (not to scale) of Product A is shown in the drawings as Figure 2a, and of Product b as Figure 2b, where a ruler is shown, indicating that the particles are about 3mm in diameter.

[0043] It should be noted that cardboard does contain somewhat rough fibres and this in theory can lead to destabilisation of an emulsion. However, if the cardboard is pelletised, this reduces the surface area sufficiently that some ammonium nitrate based emulsions can be used with it. In particular, formulations whereby the fuel phase only consists of emulsifiers and mineral oil with no diesel fuel oil present appear to be particularly suitable in this combination.

[0044] To retain the water resistance ability of the emulsion, at least 50% emulsion should be retained in the blend, although ideally it should be 60% or greater. Conversely the level of waste material can be between 1 to 50%, although preferably it will be between 10 and 40%.

[0045] A dry mix can be added to the ammonium nitrate based emulsion. The dry mix can consist of ammonium nitrate or a mixture of ammonium nitrate and diesel oil (ANFO). The dry addition, if used, comprises from 0 to 40%, by weight of the total composition. The blasting profile may be modified by the addition of ANFO, for example, by providing more heave to the blasting profile.

[0046] The waste materials preferably are pelletised so as to provide a compact structure devoid of any significant cavities in the material. As a result, the waste material provides no sensitisation and does not participate in
the explosive reaction. Furthermore, the size of the material, approximately 3mm in size, means that there is decoupling between the oxidiser and fuel. This was observed to be the case when the Product B pellets were mixed with ammonium nitrate in a ratio of 93% by weight ammonium nitrate and 7% by weight pellets. The product was fired in 223 mm diameter PVC pipes and the composition failed to detonate. Only when 1.5% of the ammonium nitrate was replaced with diesel fuel did the material detonate at low order at 1,700 m/s.

[0047] Sensitisation may be provided by the addition of a density reducing agent. Such density reducing agents can be any of the many described in the art, such as glass or plastic microballoons, occluded air or by being chemically gassed. It is preferred that the material is chemically gassed using alkali metal nitrites salts such as sodium nitrite or potassium nitrite. Typically a 20 to 30% solution of sodium nitrite is added to an acidified ammonium nitrate based emulsion. The nitrite ions are protonated and then react with the ammonium ions to generate nitrogen gas. Generation of the gas is normally completed within 20 to 60 minutes. The amount of the sodium nitrite solution used determines the final density of the explosive composition. Density of the final explosive composition should ideally be under 1.15 gm/cm³ and most preferably between 0.8 to 1.15 g/cc to ensure the composition will detonate.

[0048] Below various examples of the invention are shown. These are examples only and do not in any way limit the invention.

[0049] COMPARATIVE EXAMPLE 1 (not this invention)
In the first example, not part of this invention, TITAN™ 2000 emulsion 70% by weight was mixed with ANFO 30% by weight. The mixture was acidified with a 50% acetic acid solution and then a 25% by weight sodium nitrite solution was added to the explosive composition at 0.30% weight of the total explosive composition. This addition reduced the explosive composition from 1.32 g/cc to 1.10 g/cc. The explosive composition was loaded into 102 mm diameter PVC pipes and detonated using a 400g Pentolite booster fitted with a #12 strength detonator. A VOD of 4,000 m/s was recorded. The stability of the mixture was determined to have a Rod Rating of 6 after 28 days.
In the second example, not part of this invention, TITAN™ 2000 emulsion 80% by weight was mixed with Product B 20% by weight and no sensitisation was added. The mixture had a density of 1.17 g/cc and was loaded into 152 mm diameter PVC pipes and detonated. The product failed to detonate when initiated with a 400g Pentolite booster fitted with a #12 strength detonator. These results indicate that the Product B does not provide sensitisation to the emulsion.

The following examples show that sensitisation is required.

In the third example, TITAN™ 7000 emulsion 80% by weight was mixed with Product A at 20% by weight. The mixture was acidified with a 50% by weight acetic acid solution and then a 25% by weight sodium nitrite solution was added to the explosive composition at 0.3% by weight of the total explosive composition. This addition reduced the explosive composition from 1.27 g/cc to 1.10 g/cc. The explosive composition was loaded into 152 mm diameter PVC pipes and detonated using a 400g Pentolite booster fitted with a #12 strength detonator. A VOD of 3,800 m/s was recorded. The stability of the mixture was determined to have a Rod Rating of 6 after 20 days, and the blend breaks down after 28 days.

In a fourth example, TITAN™ 2000 emulsion 80% by weight was mixed with Product B 20% by weight. The mixture was acidified with a 50% acetic acid solution and then a 25% by weight sodium nitrite solution was added to the explosive composition at 0.2% weight of the total explosive composition. This addition reduced the explosive composition from 1.17 g/cc to 1.02 g/cc. The explosive composition was loaded into 152 mm diameter PVC pipes and detonated using a 400g Pentolite booster fitted with a #12 strength detonator. A VOD of 4,000 m/s was recorded. The stability of the mixture was determined to have a Rod Rating of 7 after 28 days.

EXAMPLE 5
In a fifth example, TITAN™ 7000 emulsion 80% by weight was mixed with Product B 20% by weight. The mixture was acidified with a 50% by weight acetic acid solution and then a 25% by weight sodium nitrite solution was added to the explosive composition at 0.2% by weight of the total explosive composition. This addition reduced the explosive composition from 1.22 g/cc to 1.03 g/cc. The explosive composition was loaded into 152 mm diameter PVC pipes and detonated using a 400g Pentolite booster fitted with a #12 strength detonator. A VOD of 5,100 m/s was recorded.

[0055] EXAMPLE 6
In a sixth example, TITAN™ 2000 emulsion 60% by weight was mixed with Product B 10% by weight and ANFO 30% by weight. The mixture was acidified with a 50% by weight acetic acid solution and then a 25% by weight sodium nitrite solution was added to the explosive composition at 0.2% by weight of the total explosive composition. This addition reduced the explosive composition from 1.23 g/cc to 1.12 g/cc. The explosive composition was loaded into 152 mm diameter PVC pipes and detonated using a 400g Pentolite booster fitted with a #12 strength detonator. A VOD of 4,500 m/s was recorded.

[0056] EXAMPLE 7
In a seventh example, TITAN™ 2000 emulsion 60% by weight was mixed with Product B 20% by weight and ANFO 20% by weight. The mixture was acidified with a 50% acetic acid solution and then a 25% by weight sodium nitrite solution was added to the explosive composition at 0.1% weight of the total explosive composition. This addition reduced the explosive composition from 1.18 g/cc to 1.10 g/cc. The explosive composition was loaded into 152 mm diameter PVC pipes and detonated using a 400g Pentolite booster fitted with a #12 strength detonator. A VOD of 4,200 m/s was recorded.

[0057] EXAMPLE 8
In an eighth example, TITAN™ 7000 emulsion 80% by weight was mixed with Product B 20% by weight. The mixture was acidified with a 50% by weight acetic acid solution and then a 25% by weight sodium nitrite solution was added to the explosive composition at 0.1% by weight of the total explosive
composition. This addition reduced the explosive composition from 1.22 g/cc to 1.15 g/cc. The explosive composition was loaded into 152 mm diameter PVC pipes and detonated using a 400g Pentolite booster fitted with a #12 strength detonator. A VOD of 4,900 m/s was recorded.

[0058] ROD RATING TESTING
Various components were tested for their stability, as indicated in Table 2. This test involved mixing the bulking agent, ANFO and/or emulsion and then monitoring the level of crystallisation in the emulsion as a function of time. This was achieved by using a 10 mm glass rod that is dipped into the blend at a 45 degree angle to a depth of approximately 20 mm to coat one side of the glass rod with blend. The glass rod is then lightly tapped to remove excess bulking agent, prill and/or emulsion. The glass rod is held toward a light source with the side coated with emulsion is facing away and allowing the light to pass through the glass rod. The emulsion is than lightly rubbed along the glass rod three times and the proportion of crystals are measured as follows:-

8 = no crystals; 7 = small amount of crystals; 6 = half emulsion/half crystals; 5 = mostly crystals with some emulsion; 4 = All crystals with no emulsion.

The blend is continually rated for the proportion of crystal formation over time at known intervals.

[0059] EXAMPLE 9 - Stability Testing
A first test was carried out, in accordance with the invention, using TITAN™ 2000 emulsion 80% by weight was mixed with Product B 20% by weight, and gassed to a density of 0.99 g/cc, and this gave a Rod Rating of 7 after 28 days.

[0060] In contrast, tests with other substances as the waste component gave inferior results for the stability of the emulsions. It is highly preferred that such emulsions must be stable for at least 14 days, and preferably are stable for 28 days. The test for stability is preferably the Rod Rating test, described herein, and a suitable stability will be an emulsion that has a Rod Rating of 6 or higher, for at least 14 days.

[0061] Results for these tests are given in Table 2, below.
<table>
<thead>
<tr>
<th>Composition</th>
<th>Density g/cc</th>
<th>Period</th>
<th>Rod Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>80% T2000 and 20% Product B (Fig 3a) (invention)</td>
<td>0.99</td>
<td>28 days</td>
<td>7</td>
</tr>
<tr>
<td>80% T2000 and 20% shredded tires (Fig 3b)</td>
<td>1.03</td>
<td>8 hours</td>
<td>&gt;4</td>
</tr>
<tr>
<td>10% comingled plastic shredded (Fig 3c), 54% T2000 and 36% ANFO - no gassing</td>
<td>0.95</td>
<td>1 day</td>
<td>4</td>
</tr>
<tr>
<td>5% comingled plastic shredded (Fig 3c), 54% T2000 and 36% ANFO - no gassing</td>
<td>1.23</td>
<td>1 day</td>
<td>4</td>
</tr>
<tr>
<td>10% HDPE pellets, 54% T2000 and 36% ANFO - no gassing</td>
<td>1.25</td>
<td>28 days</td>
<td>6</td>
</tr>
<tr>
<td>10% compacted vinyl, 54% T2000 and 36% ANFO - no gassing</td>
<td>1.21</td>
<td>5 days</td>
<td>4</td>
</tr>
</tbody>
</table>

**TABLE 2. STABILITY TESTING**

[0062] It can be seen from the microscope photographs in Figures 3a, 3b and 3c of the various waste material tested, that the material in accordance with the invention in Figure 3a has significantly smoother surfaces and edges, than with the shredded tyres in Figure 3b or comingled plastics in Figure 3c. The stability tests in Table 2 show that crystallisation occurs and the emulsion is destabilised as a result.

[0063] [0064] EXAMPLE 10 - TESTING OF BLASTING

Tests were conducted in the field, using blasting compositions having as the bulking agent the pellets in accordance with Figure 2b and 2d. A site was selected where the natural surface was drilled with shot holes.
Results for these tests are given in Table 3, below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount (kg/hole)</th>
<th>Hole Depth (m)</th>
<th>Density (g/cm³)</th>
<th>VOD (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>250</td>
<td>8 - 10</td>
<td>1.02 - 1.04</td>
<td>3000</td>
</tr>
<tr>
<td>2b</td>
<td>230 - 310</td>
<td>7 - 8</td>
<td>0.98 - 1.06</td>
<td>3800</td>
</tr>
<tr>
<td>2d</td>
<td>250</td>
<td>8</td>
<td>0.94 - 0.98</td>
<td>3900</td>
</tr>
</tbody>
</table>

TABLE 3

The blasting testing involved loading several holes the emulsion according to the invention. Three shots were tested with the results as shown in Table 3. The product detonated to high order and steady state. No fumes were observed to originate for any of the locations loaded with the blasting emulsion including the waste plastics bulking agents.

DELIVERY OF EXPLOSIVE COMPOSITION

Figure 1 shows a schematic of a truck used for the manufacture and delivery of bulk explosives into blastholes at a mine. The truck (1), which is also known as a mobile processing unit (MPU), has three sections (10, 20, 30). The first and smallest section (10) is usually for storage of fuel oil, which traditionally comprises about just 6% of the ANFO component. The second section (20) is normally used for storage of the ammonium nitrate for dry addition. The third section (30) is used for storage of the ammonium nitrate based emulsion.

It is preferable that the waste material is approximately spherical in shape and about 2 to 3 mm in size. This size and shape allows the material to have similar flow properties to ammonium nitrate for the dry addition. As a result, the waste material can be substituted into the second section (20) of the truck. The lack of fines and the flowability of the waste material allow the second section (20) to be used for either material (the waste material pellets or the AN prill) without significant contamination issues. Furthermore, the lack of sensitivity of the waste material means that even if there are some remnants of waste material in this section (20), it will not provide a source of
ignition or provide fuel for the ammonium nitrate prill. Therefore the MPU trucks can be used for either arrangement and easily re-purposed, to carry either set of blasting components.

[0069] The MPU truck (1) has an auger (40) which allows the mixing of the waste material with the emulsion. A density reducing agent can also be fed into the mixture to reduce the density of the explosive composition. If the density reducing agent is an alkaline metal nitrite salt, then a salt solution can be administered through an inlet port (not shown) into the auger arm (42). The explosive composition is delivered out the auger (40) into a blast hole (not shown).

[0070] The blasting composition according to the invention, and its method of delivery to blastholes is particularly of benefit when blasting soft, wet ground, such as natural surfaces. The invention is also of benefit when fume mitigation is of importance, as the blasts will produce a minimum about of fumes, especially of noxious NOx fumes when the nitrogen gas sensitisation is utilised in the composition.

[0071] In this specification, unless the context clearly indicates otherwise, the term "comprising" has the non-exclusive meaning of the word, in the sense of "including at least" rather than the exclusive meaning in the sense of "consisting only of". The same applies with corresponding grammatical changes to other forms of the word such as "comprise", "comprises" and so on.

[0072] Although the invention is described above with reference to specific embodiments, it will be appreciated by those skilled in the art that it is not limited to those embodiments, but may also exist in many other forms.

**INDUSTRIAL APPLICABILITY**

[0073] The invention can be utilised in industries using blasting compositions of the invention, including the mining, quarrying, and construction industries.
CLAIMS:

1. An explosive composition comprising an aqueous emulsion of
   - an oxidizer component,
   - a hydrocarbon fuel component containing emulsifier, and
   - fuel-type waste material in a solid particulate form lacking rough
   surfaces and sharp edges sufficiently so as to not promote
   crystallisation of the emulsion.

2. The composition of claim 1, wherein the presence of the waste
   material alone does not provide sensitisation to the emulsion to permit
   an explosion; an explosion being permitted by the later addition of a
   sensitisation component to the composition.

3. The composition of claim 2, wherein the sensitisation component is a
   density reducing agent.

4. The composition of claim 1, wherein the oxidizing agent is selected
   from one or more of ammonium nitrate, sodium nitrate, or calcium
   nitrate.

5. The composition of claim 4, wherein the oxidizing agent is ammonium
   nitrate.

6. The composition of claim 3, where the density reducing agent is a salt
   of an alkali metal nitrite and an acid, which generate nitrogen gas
   when combined.

7. The composition of claim 1, wherein the composition of the fuel type
   waste material is selected from any one or more of: plastics material,
   rubber, paper, cardboard, wax material, and commingled plastic waste
   material.

8. The composition of claim 6, wherein the density of the composition is
   reduced to between 0.80 and 1.15 g/cm$^3$ by the addition of the density
   reducing agent.
9. The composition of claim 1, wherein the particulate waste material is in the form of pellets substantially lacking rough surfaces and sharp edges.

10. The composition of claim 1, wherein the particulate waste material has an average particle size of about 2 to 3 mm.

11. The composition of claim 1, wherein the waste material comprises from 1% to 50% by weight of the total composition.

12. The composition of claim 11, wherein the waste material comprises from 10 to 40% by weight of the total composition.

13. The composition of claim 1, wherein the fuel-type waste material in a solid particulate form has a Rod Rating test (as described herein) value of 6 or higher.

14. A method of providing an explosive composition to a blast site having one or more blastholes for receiving the composition, by means of a conventional mobile processing unit (MPU), said unit comprising a truck having separate compartments adapted for holding (a) fuel oil, (b) dry ammonium nitrate prill, and (c) ammonium nitrate-based emulsion, and said unit having means for mixing two or more of the components from compartments (a), (b) and (c) together and injecting the resulting mixture in a blasthole, characterised in that compartment (b) instead holds particulate waste material, and a density reducing agent is added to the mixture from compartments (a), (b) and (c) just prior to it being injected into a blast hole by an auger on the MPU, and wherein the composition is as defined in any one of claims 1 to 12.

15. The method of claim 14, wherein the mixture is injected into the blasthole by means of an auger.
16. A method of blasting soft and wet ground, which comprises injecting into one or more blast holes in the soft and wet ground a sufficient quantity of the composition according to any one of claims 1 to 12, and then setting off the composition.

17. The method of claim 16, wherein the composition is injected into the blast holes by means of a conventional mobile processing unit, said unit comprising a truck having separate compartments adapted for holding (a) fuel oil, (b) dry ammonium nitrate prill, and (c) ammonium nitrate based emulsion, and said unit having means for mixing two or more of the components from compartments (a), (b) and (c) together and injecting the resulting mixture in a blasthole, characterised in that compartment (a) instead holds particulate waste material, and a density reducing agent is added to the mixture from compartments (a), (b) and (c) just prior to it being injected into a blast hole by an auger of the MPU.

18. The method of claim 17, wherein the mixture is injected into the blasthole by means of an auger.

* * * * *
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Documents are listed in the continuation of Box C

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Date of the actual completion of the international search: 10 May 2013
Date of mailing of the international search report: 10 May 2013

Name and mailing address of the ISA/All

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<tr>
<td>A</td>
<td>US 5,505,800 A (HARRIES et al) 09 April 1996 Cited in application; see abstract, examples and column 5</td>
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<tr>
<td>A</td>
<td>US 5,397,405 A (SMITH et al) 14 March 1995 See abstract</td>
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</tr>
</tbody>
</table>
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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<tr>
<td>US 5505800 A</td>
<td>AU 661675 B2</td>
</tr>
<tr>
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<td>03 Aug 1995</td>
</tr>
<tr>
<td></td>
<td>AU 1247792 A</td>
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<td></td>
<td>07 Sep 1992</td>
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<td>BR 9205622 A</td>
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<td>CA 2103792 A1</td>
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<td>12 Aug 1992</td>
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<td>EP 0571477 A1</td>
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<td>EP 0571477 B1</td>
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<td>20 May 1998</td>
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<td>FI 933522 A</td>
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<td>08 Oct 1993</td>
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<td>FI 107332 B1</td>
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<td>13 Jul 2001</td>
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<td>IN 179760 A1</td>
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<td>29 Nov 1997</td>
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<td>MX 9200576 A</td>
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<td>01 Aug 1992</td>
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<td>US 5505800 A</td>
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<td>09 Apr 1996</td>
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<td>WO 9213815 A1</td>
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<td>20 Aug 1992</td>
</tr>
<tr>
<td>US 5397405 A</td>
<td>CA 2064609 A1</td>
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<td>02 Oct 1993</td>
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<td>US 5397405 A</td>
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