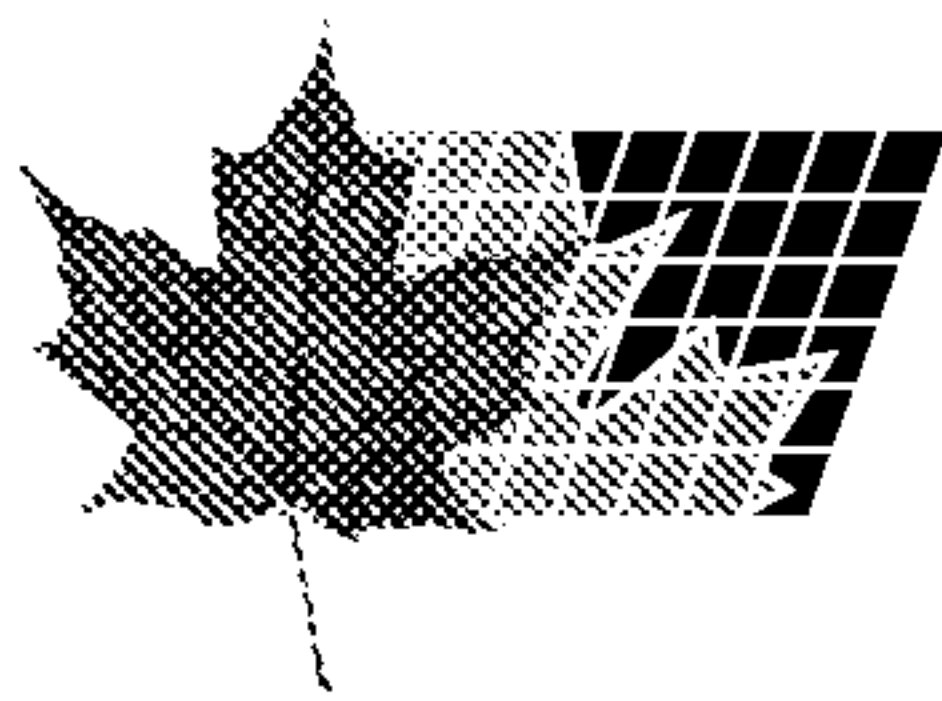




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(54) **COMPOSITION DE GAZAGE D'EXPLOSIFS ET PROCEDE
CORRESPONDANT**

(54) **EXPLOSIVES GASSER COMPOSITION AND METHOD**

(57) Cette invention se rapporte à une composition de gazage servant à gazer des compositions d'explosifs et comprenant un agent de gazage et un sel métallique contenant un cation divalent.

(57) A gassing composition for gassing explosive compositions wherein, the gassing composition comprises a gassing agent and a metal salt having a divalent cation.

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(54) Title: EXPLOSIVES GASSER COMPOSITION AND METHOD (57) Abstract A gassing composition for gassing explosive compositions wherein, the gassing composition comprises a gassing agent and a metal salt having a divalent cation.		

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EXPLOSIVES GASSER COMPOSITION AND METHOD

The present invention relates to improved chemical gassing of explosives, in particular to a gassing composition for use in explosives. The present invention also relates to a method of
5 manufacturing explosives and to an explosive composition.

Civilian mining, quarrying and excavation industries commonly use bulk or packaged explosive formulations as a principal method for breaking rocks and ore for mining, building tunnels, excavating and similar activities.

10

Chemical gassing of explosive compositions, such as emulsion explosives, has been practised with chemical gassing agents such as sodium nitrite. These gassing agents may, in certain conditions take a considerable time to generate the desired gas and form a suitable gassed explosive. In commercial operations it is desirable to quickly generate the gas so that the
15 explosive may be detonated. One of the problems associated with the gasser systems of the prior art is that the maximum gasser rate currently achievable is not sufficiently rapid for some applications. For example, this is a particular disadvantage when bulk explosives are loaded into large volume blastholes in cold climates because it may take several hours for the bulk explosive to fully gas. Attempts have been made to overcome this problem by keeping
20 the emulsion temperature very high to maintain high gasser rates however the use of high emulsion temperatures can tend to cause the emulsion to breakdown during loading into a blasthole, particularly where the emulsion is pumped into the blasthole.

It is preferable that the gasser reaction commences shortly after the mixture of gasser
25 composition and bulk emulsion is loaded into a blasthole and reaches completion rapidly. Mining operations are usually carried out on a tight schedule and delays are minimised so that efficiency is maximised. Accordingly there are economic advantages to minimising the delay between the completion of loading and detonation of the blastholes. This is particularly important in underground blasting where an entire mine tunnel may have to be evacuated and
30 activities in many areas halted while blasting is carried out. In many above ground and

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underground mines blasting is carried out at one set time each day and if the blastholes and explosives are not ready at the set time, then there is a 24 hour wait for the next opportunity to detonate the blastholes.

- 5 We have now found that improvements to the gassing of explosive compositions, including a far greater range of gassing rates and a higher maximum gassing rate, may be achieved by using one or more metal salts comprising divalent cations. Accordingly, the present invention provides a gassing composition for gassing explosive compositions wherein, the gassing composition comprises a gassing agent and a metal salt having a divalent cation.

10

The present invention further provides a method for gassing an explosive composition comprising the steps of:

- i) forming a gassing composition comprising a gassing agent and a metal salt having a divalent cation; and

15

- ii) dispersing the gassing composition into the explosive composition.

Additionally the present invention provides a gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive
20 composition wherein the gassing composition comprises a gassing agent and a metal salt having a divalent cation.

The metal salt may be any convenient salt containing a divalent metal cation and includes simple salts, double salts, complexes and any other convenient means.

25

The divalent cation may be any divalent cation of a main group metal, transition metal, lanthanide or actinide. The divalent cation may preferably be formed from a main group metal of Group II, III, IV or V or a transition metal or mixtures thereof. More preferably the divalent may be selected from the group consisting of Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Ti^{2+} ,
30 Zr^{2+} , Hf^{2+} , V^{2+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^{2+} , Hg^{2+} , Cd^{2+} , Al^{2+} , Sn^{2+} ,

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Pb^{2+} and mixtures thereof. The most preferred divalent metal cations are Mg^{2+} and Ca^{2+} .

The anion or anions, of the metal salt may be any suitable monovalent, divalent or trivalent
5 anion. The metal salt may comprise more than one monovalent anion. The metal salt may be
a double salt. Preferably the anion of the metal salt may be selected from the group consisting
of halide, nitrate, sulphate, phosphate, chlorate, perchlorate and combinations thereof. More
preferably the anion of the metal salt is nitrate.

10 The gassing composition may be in any convenient form, preferably in the form of a solution.
The solution may be dispersed within the explosive or may be first put in the form of a water-
in-oil emulsion, oil-in-water emulsion, foamed emulsion, microemulsion or combination
thereof to facilitate dispersal of the gassing composition in the explosive composition.
Typically the gassing composition comprises a chemical gassing agent and a divalent metal
15 salt dissolved in a solvent or mixture of solvents. The solvent may be any suitable liquid in
which the chemical gasser agent and divalent metal salt are soluble, such as water.
Advantageously, the gasser composition may be formed from separate solutions of gassing
agent and metal salt, which solutions are blended immediately prior to their dispersal in the
explosive.

20

The gassing agent is an agent suitable for the in situ chemical generation of gas bubbles and
includes peroxides such as hydrogen peroxide, nitrite salts such as sodium nitrite and
potassium nitrite, nitrosamines such as N,N'-dinitrosopentamethylenetetramine, diazonium
ions/salts, alkali metal borohydrides such as sodium borohydride and bases such as carbonates
25 including sodium carbonate.

Nitrite salts, and more preferably sodium nitrite, are preferred for use in the present
invention. The nitrite salts react under conditions of acid pH to produce nitrogen gas bubbles.

30 Accelerators such as thiocyanate salts, iodides, sulphamic acid or its salts or thiourea may be

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used in the gassing composition to accelerate the gassing reaction.

Typically the gassing composition of the present invention may comprise gassing agent between 0.5 wt% and 45 wt% of the gassing composition and divalent metal salt between 1
5 wt% and 45 wt% of the gassing composition. Preferably the gassing composition comprises between 0.5 wt% and 25 wt% gassing agent and between 10 wt% and 40 wt% divalent metal salt. More preferably the gasser composition comprises between 0.5 wt% and 20 wt% gassing agent and between 20 wt% and 40 wt% divalent metal salt. Optional accelerator, such as thiocyanate, may be present in the gassing composition at levels of between 0.05 wt% and
10 20 wt% of the gassing composition and preferably between 0.5 wt% and 10 wt%.

The gassing of the explosive compositions may preferably be carried out by forming a gassing composition by dissolving the gassing agent, the metal salt having a divalent cation and any optional additives in a solvent and dispersing the gasser composition evenly throughout the
15 explosive composition. The gassing composition subsequently reacts to generate gas bubbles in the explosive composition.

The gassing composition may be dispersed in the explosive composition at a level of between 0.5 and 10 wt% of the total composition or more typically between 0.5 wt% and 5 wt%.
20

The gassing composition of the present invention may be used in a wide variety of explosive compositions, including water-in-oil emulsions, oil-in-water emulsions (or slurries). Water-in-oil emulsions include, for example compositions where the emulsion is a water-in-oil emulsion, melt-in-fuel emulsion and melt-in-oil emulsion. The present invention will now
25 be described in relation to water-in-oil emulsion explosives. However those skilled in the art will readily understand that the gassing compositions may be used in other forms of explosive compositions with modifications adapted to account for the chemical interactions between the gasser composition and the explosive composition.

30 The rate of gas formation by a gasser composition dispersed in an emulsion may be affected

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by a variety of parameters including the emulsion temperature, ambient temperature, ground temperature, the concentration of components in the gasser composition, the composition of the explosive composition and so forth.

- 5 Water-in-oil emulsion explosive compositions were first disclosed by Bluhm in United States Patent 3,447,978 and comprise (a) a discontinuous aqueous phase comprising discrete droplets of an aqueous solution of inorganic oxygen-releasing salts; (b) a continuous water-immiscible organic phase throughout which the droplets are dispersed and (c) an emulsifier which forms an emulsion of the droplets of oxidiser salt solution throughout the continuous organic phase.
- 10 Where these types of emulsions comprise very little water or adventitious water only in the discontinuous phase they are more correctly referred to as melt-in-fuel emulsion explosives.

Preferably the emulsion suitable for use as an explosives emulsion is a water-in-oil or melt-in-oil emulsion or melt-in-fuel emulsion. Suitable oxygen releasing salts for use in the aqueous

15 phase of the emulsion of the present invention include the alkali and alkaline earth metal nitrates, chlorates and perchlorates, ammonium nitrate, ammonium chlorate, ammonium perchlorate and mixtures thereof. The preferred oxygen releasing salts include ammonium nitrate, sodium nitrate and calcium nitrate. More preferably the oxygen releasing salt comprises ammonium nitrate or a mixture of ammonium nitrate and sodium or calcium

20 nitrates.

Typically the oxygen releasing salt component of the compositions of the present invention comprise from 45 to 95 wt% and preferably from 60 to 90 wt% of the total emulsion composition. In compositions wherein the oxygen releasing salt comprises a mixture of

25 ammonium nitrate and sodium nitrate or calcium nitrate the preferred composition range for such a blend is from 5 to 100 parts of sodium nitrate or calcium nitrate for every 100 parts of ammonium nitrate.

Typically the amount of water employed in the compositions of the present invention is in the

30 range of from 0 (for a melt-in-fuel emulsion) to 30 wt% of the total emulsion composition.

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Preferably the amount employed is from 4 to 25 wt% and more preferably from 6 to 25 wt%.

The continuous water immiscible organic phase of the emulsion composition of the present invention comprises the continuous "oil" phase of the emulsion composition and is the fuel.

5 Suitable organic fuels include aliphatic, alicyclic and aromatic compounds and mixtures thereof which are in the liquid state at the formulation temperature. Suitable organic fuels may be chosen from fuel oil, diesel oil, distillate, furnace oil, kerosene, naphtha, vegetable oils, waxes such as microcrystalline wax, paraffin wax and slack wax, paraffin oils, benzene, toluene, xylenes, asphaltic materials; polymeric oils such as the low molecular weight

10 polymers of olefines, animal oils, fish oils and other mineral, hydrocarbon or fatty oils and mixtures thereof. Preferred organic fuels are liquid hydrocarbons generally referred to as petroleum distillates such as gasoline, kerosene, fuel oils and paraffin oils.

Typically the organic fuel or continuous phase of the emulsion comprises from 2 to 15 wt% and preferably 3 to 10 wt% of the total composition.

15

In emulsion explosives, emulsifiers are used to decrease interfacial tension between the aqueous and oil phases. Molecules of the emulsifier locate at the interface between the aqueous droplet and continuous hydrocarbon phase. The emulsifier molecules are oriented

20 with the hydrophilic head group in the aqueous droplet and the lipophilic tail in the continuous hydrocarbon phase. Emulsifiers stabilise the emulsion, inhibiting coalescence of the aqueous droplets and phase separation. Emulsifiers also inhibit crystallisation of oxidiser salt in the aqueous droplets which crystallisation can lead to emulsion breakdown and reduction in detonation sensitivity of the emulsion explosive composition.

25

The emulsifier of the emulsion composition of the present invention may comprise emulsifiers chosen from the wide range of emulsifiers known in the art for the preparation of emulsion explosive compositions. It is particularly preferred that the emulsifier used in the emulsion composition of the present invention is one of the well known emulsifiers based on the

30 reaction products of poly[alk(en)yl] succinic anhydrides and alkylamines, including the

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polyisobutylene succinic anhydride (PiBSA) derivatives of alkanolamines. Particularly preferred emulsifiers include condensation products of poly[alk(en)yl] succinic anhydride with amines such as ethylene diamine, diethylene triamine and ethanolamine. Another preferred emulsifier for use in the emulsion composition of the present invention is a mixture of PiBSA based and sodium mono-oleate based emulsifiers. Other suitable emulsifiers for use in the emulsion of the present invention include alcohol alkoxylates, phenol alkoxylates, poly(oxyalkylene)glycols, poly(oxyalkylene)fatty acid esters, amine alkoxylates, fatty acid esters of sorbitol and glycerol, fatty acid salts, sorbitan esters, poly(oxyalkylene) sorbitan esters, fatty amine alkoxylates, poly(oxyalkylene)glycol esters, fatty acid amines, fatty acid amide alkoxylates, fatty amines, quaternary amines, alkyloxazolines, alkenyloxazolines, imidazolines, alkylsulphonates, alkylarylsulphonates, alkylsulphosuccinates, alkylarylsulphonates, alkylsulphosuccinates, alkylphosphates, alkenylphosphates, phosphate esters, lecithin, copolymers of poly(oxyalkylene)glycols and poly(12-hydroxystearic)acid and mixtures thereof.

15

Typically the emulsifier of the emulsion comprises up to 5 wt% of the emulsion. Higher proportions of the emulsifying agent may be used and may serve as supplemental fuel for the composition but in general it is not necessary to add more than 5 wt% of emulsifying agent to achieve the desired effect. Stable emulsions can be formed using relatively low levels of emulsifier and for reasons of economy it is preferable to keep the amount of emulsifying agent used at the minimum required to form the emulsion. The preferred level of emulsifying agent used is in the range of from 0.1 to 3.0 wt% of the water-in-oil emulsion.

If desired, other optional fuel materials, hereinafter referred to as secondary fuels may be incorporated into the emulsion in addition to the water immiscible organic fuel phase. Examples of such secondary fuels include finely divided solids and water miscible organic liquids which can be used to partially replace water as a solvent for the oxygen releasing salts or to extend the aqueous solvent for the oxygen releasing salts. Examples of solid secondary fuels include finely divided materials such as sulphur, aluminium, urea and carbonaceous materials such as gilsonite, comminuted coke or charcoal, carbon black, resin acids such as

30

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abietic acid, sugars such as glucose or dextrose and vegetable products such as starch, nut meal, grain meal and wood pulp. Examples of water miscible organic liquids include alcohols such as methanol, glycols such as ethylene glycol, amides such as formamide and urea and amines such as methylamine.

5

Typically the optional secondary fuel component of the composition of the present invention comprises from 0 to 30 wt% of the total composition.

Generally the emulsions themselves are not detonable and to form an explosive emulsion must
10 be mixed with sensitising agents such as a self explosive (e.g. trinitrotoluene or nitroglycerine) or a discontinuous phase of void agents. Sensitising using this explosives has been superseded by sensitisation methods which utilise nonexplosive sensitising agents. For example the incorporation of small voids into the emulsion which act as hot spots for propagating detonation may sensitize the emulsion and result in a detonable explosive.

15

There may also be incorporated into the emulsion other substances or mixtures of substances which are oxygen releasing salts or which are themselves suitable as explosive materials. For example the emulsion may be mixed with prilled or particulate ammonium nitrate or ammonium nitrate/fuel oil mixtures to form so-called heavy ANFOs (or HANFOs).

20

It will be readily apparent to those skilled in the relevant technology however that certain divalent cation salts falling within the above description may have the desired effect on the gasser rate of an emulsion, but may be less preferred for use in a gasser solution or an emulsion explosives formulation. For example, the addition of FeSO_4 to an emulsion
25 explosive formulation comprising nitrate ions may cause production of large quantities of noxious fumes. Copper nitrate may also be an unsuitable additive in an emulsion explosive formulation due to the possibility of forming undesirable by-products, including a touch sensitive explosive such as copper tetramine nitrate. Some salts such as iron nitrate and aluminium nitrate may be unsuitable if added to an emulsion explosive formulation in
30 quantities which reduce pH of the gasser solution to an undesirable level.

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The final density of the gassed emulsion may depend on the concentration of the components of the gasser composition but typically the final density is between 0.2 and 1.5 g/cc. Preferably the final density is between 0.5 and 1.3 g/cc or more preferably between 0.6 and 1.2 g/cc.

5

The water-in-oil emulsion composition may be prepared by a number of different methods. One preferred method of manufacture includes: dissolving said oxygen releasing salts in water at a temperature above the fudge point of the salt solution, preferably at a temperature in the range from 20 to 110 °C to give an aqueous salt solution; combining an aqueous salt solution,
10 a water immiscible organic phase, and an emulsifier with rapid mixing to form a water-in-oil emulsion; and mixing until the emulsion is uniform.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will
15 be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The invention is now demonstrated by but in no way limited to the following examples.

20 Example 1

In this example a number of different divalent salts were used in gasser compositions of the current invention which were added to portions of a water-in-oil emulsion. The rate of gassing of each portion of emulsion was then measured.

25 Preparation of a Water-in-Oil Emulsion

A water-in-oil emulsion of the following composition was prepared for use in the example;

Oxidiser Solution - 91 % w/w comprising

ammonium nitrate (78.9 % w/w)

water (20.7 % w/w)

30 buffer (0.4 % w/w)

- 10 -

Fuel Phase - 9 % w/w comprising a hydrocarbon oil/emulsifier mixture.

The emulsifier system comprised a mixture of a sorbitan mono-oleate derivative (SMO) and the uncondensed amide formed by the reaction of an alkanolamine with
5 poly(isobutylene)succinic anhydride (PiBSA). The emulsion was prepared by dissolving ammonium nitrate in the water at elevated temperature (98°C) then adjusting the pH of the oxidiser solution so formed to 4.2. The fuel phase was then prepared by melting the microcrystalline wax and mixing it with the hydrocarbon oil/emulsifier system mixture. The oxidiser phase was then added in a slow stream to the fuel phase 98°C with rapid stirring to
10 form a homogeneous water-in-oil emulsion.

The emulsion was then divided into numerous portions of equal mass.

Preparation of Gasser Compositions

15 A series of gasser compositions were prepared by dissolving sodium nitrite and a divalent metal salt in water. All the gasser compositions comprised 5 wt% sodium nitrite and 35 wt% divalent salt (with the exception of calcium chloride which was 32.5 wt% and magnesium sulphate which was 33.6 wt%). A control gasser composition was prepared by dissolving sodium nitrite (5 wt%) in water.

20

Addition of the Gasser Compositions to the Emulsion

The water-in-oil emulsion was divided into numerous portion. Each of the gasser compositions was mixed into a separate portion of emulsion at 30°C, the gassing rate was measured and the relative rate constant at 30°C was calculated. The relative rate constant is
25 the rate constant measured, divided by the rate constant for the control sample. The relative reaction rate constants for gasser compositions having different divalent metal salts are recorded in Table 1.

TABLE 1:

- 11 -

	Metal Salt in Gasser	Relative Rate Constant, k
	Control (no divalent metal salt)	1.0
	Sodium nitrate (NaNO_3)	0.9
5	Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)	4.4
	Calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$)	4.1
	Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$)	1.8
10	Manganese(II)nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$)	6.4
	Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)	3.4
15	Calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$)	2.7
	Magnesium sulphate ($\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$)	1.6

The results in Table 1 show that the gasser compositions comprising divalent metal salts greatly increased the gasser rate compared to gasser compositions comprising monovalent metal salts or no metal salts. The presence of a divalent metal salt in a gasser composition appears to increase the gasser rate by up to six times. It is noted in particular that the gasser composition comprising the monovalent metal salt (sodium nitrate) and sodium nitrite gasses at a slower rate than the gasser composition which comprises sodium nitrite alone. It would appear therefore, that the presence of a monovalent metal salt may depress reaction rate.

Furthermore, for salts the catalytic effect decreases going down a column of the periodic table; for example magnesium nitrate has a greater effect per mole than calcium nitrate which in turn has a greater effect than strontium nitrate. Across a row of the periodic table, magnesium and zinc nitrate have a greater effect on gasser rate than calcium nitrate. These

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results tend to suggest that the increase in gassing rate appears to be approximately inversely proportional to the formula weight of the salt or the cation size.

Example 2

- 5 In this example a gasser composition of the present invention was added to a water-in-oil emulsion comprising a PiBSA based emulsifier system and compared with the results obtained in Example 1 where the gasser composition is added to an emulsion comprising a mixed PiBSA/SMO based emulsifier system.

10 Preparation of a Water-in-Oil Emulsion

A water-in-oil emulsion was prepared as described in Example 1 but instead of a PiBSA/SMO emulsifier system, PiBSA alone was used as emulsifier. Emulsion of this formulation was suitable for use in forming an explosives emulsion.

15 Preparation of Gasser Composition

Two gasser compositions were prepared. The first gasser composition comprised 35 wt% calcium nitrate and 5 wt% sodium nitrite in water. The second, control gasser composition comprised 5 wt% sodium nitrite in water.

20 Addition of the Gasser Compositions to the Emulsion

The water-in-oil emulsion was divided into two portions. Each of the two gasser compositions were mixed into separate portions of emulsion at 30 °C, the gasser rate was measured and the relative rate constant at 30 °C was calculated. The relative rate constant is the rate constant measured, divided by the rate constant measured for the control sample. The reaction rate

- 25 constants for two gasser compositions are recorded in Table 2.

TABLE 2:

Metal Salt in Gasser	Relative Rate Constant, k
Control (no divalent metal salt)	1

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Calcium nitrate (Ca(NO ₃) ₂ ·4H ₂ O)	2.5
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The presence of the divalent metal salt (calcium nitrate) in the gasser composition increased the rate of gasser by 2.5 times the rate of gasser using the control gassing composition. It is noted that the gassing rate for the emulsion comprising PiBSA based emulsifier was less than the gassing rate for the equivalent emulsion comprising a mixed PiBSA/SMO emulsifier system (Table 1).

10 Example 3

In this example the rate of reaction by gasser compositions of the current invention comprising a divalent metal salt and/or an accelerator were compared.

Preparation of a Water-in-Oil Emulsion

15 A water-in-oil emulsion was prepared as described in Example 1.

Addition of the Gasser Compositions to the Emulsion

A series of gasser compositions were prepared and added to separate portions of the water-in-oil emulsion. Each of the two gasser compositions were mixed into separate portions of emulsion at 30 °C, the reaction rate was measured and the rate constant at 30 °C was calculated. The relative rate constant is the rate constant measured, divided by the rate constant for the control sample. The relative reaction rate constants for two gasser compositions are recorded in Table 3.

TABLE 3:

Gasser Composition	Relative Rate Constant, k
Control - 5 wt% NaNO ₂ , no NaSCN, no divalent metal salt	1.0
5 wt% NaNO ₂ 10 wt% NaSCN	1.2
5 wt% NaNO ₂ 35 wt% Ca(NO ₃) ₂ ·4H ₂ O	4.1
5 wt% NaNO ₂ 10 wt% NaSCN 35 wt% Ca(NO ₃) ₂ ·4H ₂ O	10.0

15 It is noted that for each of the four samples, the final density of the gassed emulsion was 1.0 ± 0.1 g/cc.

The results in Table 3 show that addition of thiocyanate alone to a solution of sodium nitrate gasser composition only marginally increases the reaction rate. Thiocyanate alone is a relatively poor gasser catalyst. However, when thiocyanate is added to a gasser composition comprising a divalent metal salt, there is a substantial increase in reaction rate; The reaction rate rises to around ten times the rate of gasser using the control and 2.5 times faster than using a divalent metal salt alone.

25 Example 4

The experiments described in Example 3 which were carried out at 30 °C were repeated using emulsion and gasser composition at 5 °C. The gassing rate for a gasser composition comprising divalent metal salt and thiocyanate was still 10 times the reaction rate using the control and 2.5 times faster than the reaction rate using a gasser composition comprising a divalent metal salt alone.

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Example 5

The gassing times were also measured for the experiments described in Example 3 and the results are recorded in Table 4. The gassing time is the length of time taken for the gasser reaction to reach completion in an emulsion at 30°C.

5

TABLE 4:

Gasser Composition	Gassing Time
Control - 5 wt% NaNO ₂ , no NaSCN, no divalent metal salt.	60 minutes
10 5 wt% NaNO ₂ 10 wt% NaSCN	52 minutes
5 wt% NaNO ₂ 35 wt% Ca(NO ₃) ₂ · 4H ₂ O	17 minutes
15 5 wt% NaNO ₂ 10 wt% NaSCN 35 wt% Ca(NO ₃) ₂ · 4H ₂ O	8 minutes

The results in Table 4 show that very fast gasser times can be obtained using the gassing composition of the present invention.

20

Example 6

Gasser compositions were made up using 5 wt% NaNO₂ and a range of different concentrations of divalent cation salts. The gasser compositions were added to separate portions of emulsion made according to Example 1 and the gasser rate was measured. The reaction rates measured indicate that the extent of the increase in gasser rate is approximately proportional to the square of the nitrite salt concentration. Without wishing to be bound by theory it is believed that the divalent cation takes part twice in the rate limiting step of the gassing reaction mechanism.

25

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Example 7

In this example gasser compositions of the present invention comprising different levels of divalent cation salt were added to a water-in-oil emulsion comprising a PiBSA/SMO based emulsifier system and the final gassed emulsion densities were measured.

Preparation of a Water-in-Oil Emulsion

A water-in-oil emulsion was prepared as described in Example 1.

10 Preparation of Gasser Composition

Gasser compositions of the following compositions were prepared:

TABLE 5:

	Gasser Composition	Emulsion Density, g/cc
15	Control - 5wt% NaNO_2 no NaSCN , no divalent metal salt	0.98
	5 wt% NaNO_2 10 wt% $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.97
20	5 wt% NaNO_2 15 wt% $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.98
	5 wt% NaNO_2 25 wt% $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.98
25	5 wt% NaNO_2 30 wt% $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.97

The results indicate that the level of divalent cation addition has negligible effect on the final emulsion density.

Example 8

30 The experiment described in Example 7 was repeated, the only difference being that all gasser

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compositions additionally included 10 wt% NaSCN. The densities measured for the gassed emulsions were all within the range 0.97-0.98 g/cc.

Accordingly, different levels of divalent cation salt in a gasser solution comprising sodium nitrite and sodium thiocyanate had no effect on the final density of the gassed emulsion.

Example 9

The samples of the emulsion of Example 1 at 26°C were mixed with 2.9wt% of gasser compositions of the following formulas;

10

Gasser Component	Control	Gasser Composition T1	Gasser Composition T2
NaNO ₂ (wt%)	15	15	15
NaSCN (wt%)	15	15	15
Ca(NO ₃) ₂ (wt%)	0	5	10
Water (wt%)	70	65	60

15

Gasser Compositions T1 and T2 comprise a divalent cation Ca²⁺ while the control gasser does not comprise a divalent cation.

20 The three samples of gasser composition mixed with emulsion were pumped into three separate vessels of equal volume at a loading rate of 70kg/minute.

The change in density versus time for each sample of gassed emulsion is depicted in Figure 1. Figure 1 illustrates a faster gasser rate and lower final density for the emulsion samples gassed with gasser compositions T1 and T2 than the control samples. Gasser composition T2, which comprises twice the content of divalent cation Ca²⁺ compared to gasser composition T1 also exhibits the faster gasser rate.

While the invention has been explained in relation to its preferred embodiments it is to be

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understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

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CLAIMS

1. A gassing composition for gassing explosive compositions wherein, the gassing composition comprises a gassing agent and a metal salt having a divalent cation.
2. A gassing composition according to claim 1 wherein the cation is selected from the group consisting of any divalent cation of a main group metal, transition metal, lanthanide or actinide.
3. A gassing composition according to claim 1 wherein the divalent may be selected from the group consisting of Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Ti^{2+} , Zr^{2+} , Hf^{2+} , V^{2+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^{2+} , Hg^{2+} , Cd^{2+} , Al^{2+} , Sn^{2+} , Pb^{2+} .
4. A gassing composition according to claim 1 wherein divalent metal cation is selected from the group consisting of Mg^{2+} and Ca^{2+} .
5. A gassing composition according to any one of claims 1 to 4 wherein the anion, or anions, of the metal salt are selected from the group consisting of halide, nitrate, sulphate, phosphate, chlorate, perchlorate and combinations thereof.
6. A gassing composition according to claim 5 wherein the anion, or anions, of the metal salt is nitrate.
7. A gassing composition according to any one of claims 1 to 6 wherein the gassing agent is a nitrite salt.
8. A gassing composition according to claim 7 wherein the gassing agent is a sodium nitrite.
9. A gassing composition according to any one of claims 1 to 8 wherein the gassing agent and the metal salt are in the form of a solution.

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10. A gassing composition according to any one of claims 1 to 9 wherein said gassing composition comprises gassing agent between 0.5 wt% and 45 wt% of the gassing composition and divalent metal salt between 1 wt% and 45 wt% of the gassing composition.
11. A gassing composition according to claim 10 wherein said gassing composition comprises between 0.5 wt% and 25 wt% gassing agent and between 10 wt% and 40 wt% divalent metal salt.
12. A gassing composition according to claim 11 wherein said gassing composition comprises between 0.5 wt% and 20 wt% gassing agent and between 20 wt% and 40 wt% divalent metal salt.
13. A gassing composition according to any one of claims 1 to 12 wherein the explosive composition is a water-in-oil emulsion explosive.
14. A gassing composition according to any one of claims 1 to 13 further comprising a thiocyanate salt.
15. A gassing composition according to claim 14 wherein the thiocyanate salt is sodium thiocyanate.
16. A gassing composition according to any one of claims 1 to 15 when used to gas an explosive composition wherein at least part of said explosive compositions has an acid pH of at least 4.2.
17. A gassing composition according to any one of claims 1 to 15 when used to gas a water-in-oil emulsion wherein the water-in-oil emulsion comprises an aqueous phase having an acid pH of at least 4.2.

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18. A method for gassing an explosive composition comprising the steps of:
- i) forming a gassing composition comprising a gassing agent and a metal salt having a divalent cation; and
 - ii) dispersing the gassing composition into the explosive composition.
19. A method for gassing an explosive composition according to claim 18 wherein the cation is selected from the group consisting of any divalent cation of a main group metal, transition metal, lanthanide or actinide.
20. A method for gassing an explosive composition according to claim 18 wherein the divalent may be selected from the group consisting of Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Ti^{2+} , Zr^{2+} , Hf^{2+} , V^{2+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^{2+} , Hg^{2+} , Cd^{2+} , Al^{2+} , Sn^{2+} , Pb^{2+} .
21. A method for gassing an explosive composition according to claim 18 wherein divalent metal cation is selected from the group consisting of Mg^{2+} and Ca^{2+} .
22. A method for gassing an explosive composition according to any one of claims 18 to 21 wherein the anion, or anions, of the metal salt are selected from the group consisting of halide, nitrate, sulphate, phosphate, chlorate, perchlorate and combinations thereof.
23. A method for gassing an explosive composition according to claim 22 wherein the anion, or anions, of the metal salt is nitrate.
24. A method for gassing an explosive composition according to any one of claims 18 to 23 wherein the gassing agent is a nitrite salt.

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25. A method for gassing an explosive composition according to claim 24 wherein the gassing agent is a sodium nitrite.
26. A method for gassing an explosive composition according to any one of claims 18 to 25 wherein the gassing agent and the metal salt are in the form of a solution.
27. A method of gassing an explosive composition according to any one of claims 1 to 26 wherein the gassing composition is dispersed into the explosive composition by the use of static mixers whilst the explosive composition is being pumped.
28. A method of gassing an explosive composition according to claim 27 wherein the explosive composition is a water-in-oil emulsion explosive.
29. A method for gassing an explosive composition according to any one of claims 18 to 28 wherein the gassing composition further comprises a thiocyanate salt.
30. A method for gassing an explosive composition according to claim 29 wherein the thiocyanate salt is sodium thiocyanate.
31. A method for gassing an explosive composition according to any one of claims 1 to 30 wherein at least part of said explosive composition has an acid pH of at least 4.2.
32. A method for gassing an explosive composition according to any one of claims 1 to 30 wherein the explosive composition is a water-in-oil emulsion, which emulsion comprises an aqueous phase having an acid pH of at least 4.2.
33. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition wherein the gassing composition comprises a gassing agent and a metal salt having a divalent cation.

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34. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to claim 33 wherein the cation is selected from the group consisting of any divalent cation of a main group metal, transition metal, lanthanide or actinide.
35. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to claim 33 wherein the divalent may be selected from the group consisting of Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Ti^{2+} , Zr^{2+} , Hf^{2+} , V^{2+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^{2+} , Hg^{2+} , Cd^{2+} , Al^{2+} , Sn^{2+} , Pb^{2+} .
36. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to claim 33 wherein divalent metal cation is selected from the group consisting of Mg^{2+} and Ca^{2+} .
37. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to any one of claims 33 to 36 wherein the anion, or anions, of the metal salt are selected from the group consisting of halide, nitrate, sulphate, phosphate, chlorate, perchlorate and combinations thereof.
38. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to claim 37 wherein the anion, or anions, of the metal salt is nitrate.
39. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to any one of claims 33 to 38 wherein the gassing agent is a nitrite salt.

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40. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to claim 39 wherein the gassing agent is a sodium nitrite.
41. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to any one of claims 33 to 40 wherein the gassing agent and the metal salt are in the form of a solution.
42. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to any one of claims 33 to 41 wherein said gassing composition comprises gassing agent between 0.5 wt% and 45 wt% of the gassing composition and divalent metal salt between 1 wt% and 45 wt% of the gassing composition.
43. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to claim 42 wherein said gassing composition comprises between 0.5 wt% and 25 wt% gassing agent and between 10 wt% and 40 wt% divalent metal salt.
44. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to claim 43 wherein said gassing composition comprises between 0.5 wt% and 20 wt% gassing agent and between 20 wt% and 40 wt% divalent metal salt.
45. A gassed explosive composition comprising an explosive composition gassed by dispersing a gassing composition into said explosive composition according to any one of claims 33 to 44 wherein the explosive composition is a water-in-oil emulsion explosive.

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46. A gassed explosive composition according to any one of claims 33 to 45 wherein the gassing composition further comprises a thiocyanate salt.
47. A gassed explosive composition according to claim 46 wherein the thiocyanate salt is sodium thiocyanate.
48. A gassed explosive composition according to any one of claims 33 to 47 wherein at least part of said explosive composition has an acid pH of at least 4.2 prior to gassing.
49. A gassed explosive composition according to any one of claims 33 to 47 wherein the water-in-oil emulsion comprises an aqueous phase having an acid pH of at least 4.2.
50. An emulsion explosive composition comprising an organic fuel as a continuous phase; an inorganic oxidizer salt solution or melt as a discontinuous phase; an emulsifier; and gas bubbles formed from a chemical gassing agent that comprises a nitrite salt and an ion selected from the group consisting of calcium ion, strontium ion and mixtures thereof as a gassing enhancer.
51. An explosive composition according to claim 1 wherein the ion is calcium ion.
52. An explosive composition according to claim 1 wherein the ion is strontium ion.
53. An explosive composition according to any one of claims 50 to 52 wherein the emulsifier is an alkanolamine or polyol derivative of a carboxylated or anhydride derivatized olefinic or vinyl addition polymer.
54. An explosive composition according to either claim 51 or 53 wherein the calcium ion is selected from the group consisting of calcium nitrite, calcium nitrate, calcium thiocyanate and mixtures thereof.

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55. An explosive composition according to either claim 52 or 53 wherein the strontium ion is selected from the group consisting of strontium nitrite, strontium nitrate, strontium thiocyanate and mixtures thereof.
56. An explosive composition according to claim 54 wherein the calcium ion is from calcium nitrite.
57. A method for gassing an emulsion explosive composition comprising adding to a pre-formed emulsion phase a chemical gassing agent containing a nitrite salt and an ion selected from the group consisting of calcium ion, strontium ion and mixtures thereof and mixing the gassing agent uniformly throughout the emulsion phase to produce sensitizing gas bubbles.
58. A method according to claim 57 wherein the ion is calcium ion.
59. A method according to claim 57 wherein the ion is strontium ion.
60. A method according to any one of claims 57 to 59 wherein the emulsifier is an alkanolamine or polyol derivative of a carboxylated or anhydride derivatized olefinic or vinyl addition polymer.
61. A method according to either claim 58 or 60 wherein the calcium ion is selected from the group consisting of calcium nitrite, calcium nitrate, calcium thiocyanate and mixtures thereof.
62. A method according to either claim 59 or 60 wherein the strontium ion is selected from the group consisting of strontium nitrite, strontium nitrate, strontium thiocyanate and mixtures thereof.
63. A method according to claim 61 wherein the calcium ion is from calcium nitrite.

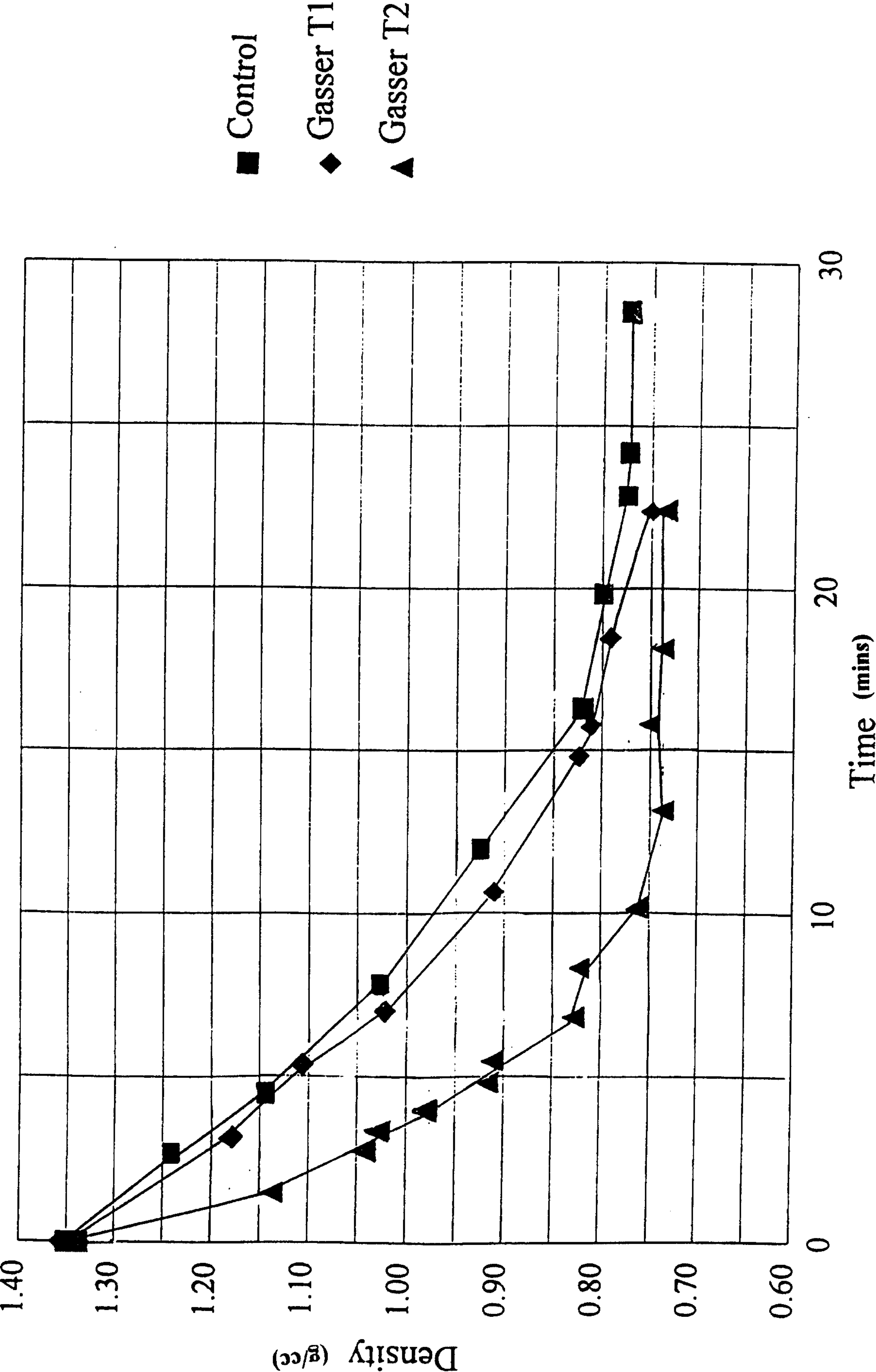


FIGURE 1