ABSTRACT

An explosive composition containing an inorganic oxidizer salt, a water soluble fuel, a metallic water insoluble fuel, water and sensitizing particles which contain encapsulated gas. The particles contain an additional fuel component which may be located either on the surface of the particles or within the encapsulating material itself. Part of the gaseous component is capable of reacting with the fuel component of the encapsulating particle.

10 Claims, No Drawings
EXPLOSIVE COMPOSITIONS WITH COATED GASEOUS ENCAPSULATIONS

This invention relates to new compositions of matter and in particular it relates to new explosive compositions of matter.

Explosive compositions in the form of slurries and comprising inorganic oxidizing salts, fuel and water, optionally together with conventional thickeners, cross-linking promoters and cross-linking retardants are known. Whilst such compositions have in the main been satisfactory for use as explosives it has been found that they suffer from the disadvantage of being too insensitive for certain applications. Furthermore the sensitivity of such compositions tends to be variable from batch to batch of production; in particular the sensitivity of such compositions tends to diminish from the original value during prolonged storage or after pumping into boreholes. So as to overcome this disadvantage it has been proposed to add an amount of gas such as air or carbon dioxide to such compositions prior to use or to generate gas in the composition in situ in the borehole. However, when compositions containing added gas are pumped into a borehole the original sensitivity of the composition is not maintained in the borehole. When the gas is generated in situ or is present as added gas in the composition it has been found when the borehole is of considerable depth, say from 20 to 100 feet deep, that the gas is compressed and becomes less effective in promoting sensitivity to the composition.

We have now found that the sensitivity to detonation of an explosive composition may be enhanced if there are incorporated into said composition water insoluble particles having a gas or a mixture of gases encapsulated within their interior and characterized further in that they have encapsulated within their interior or incorporated within their wall structure or attached to their outer surface fuel material as hereinafter defined. The particles may also be made of water insoluble fuel material.

Accordingly we provide explosive compositions of matter comprising firstly at least one oxygen releasing salt selected from the group consisting of inorganic nitrates, chlorates and perchlorates; secondly, water; thirdly, at least one fuel; and fourthly an sensitizers and oxidative additives water insoluble particles having gas or a mixture of gases encapsulated within their interior and characterized further in that they comprise fuel material as hereinafter defined.

The particulate material comprising fuel material used in the compositions according to our invention may be formed from materials of a diverse nature. Thus the particles or granules may be formed from inorganic or organic materials. For example, in one embodiment of our invention the particles may be made from a metal or an alloy of metals which is a fuel material suitable for use in our compositions, or they may be made from glass compositions comprising metallic particles suitable for use as a fuel. The manufacture of such hollow, monocular or balloon like particles is well known. Thus for example hollow glass beads can be made by mixing glass fines, admixed with finely divided metal, with a small amount of a foaming agent and sintering to the maximum density. After comminution of the sintered mass the fragments are sized, mixed with an inert paring substance which prevents fusion and subjected to temperatures at the melting point of the glass for several hours. The hollow micro balloons so formed are annealed slowly to prevent fracture. Suitable particles may also be prepared by coating glass spheres on their outer surface with water insoluble fuels.

In another embodiment of our invention the particles comprising fuel material may be made from plastics materials which may be homopolymeric or copolymeric materials or condensation products optionally containing conventional plasticizers, fillers, pigments and reinforcing agents. The means of preparing hollow polymeric plastic particles from polymers such as polyvinylidenchloride or copolymers of vinylidene-chloride with lesser amounts of other compounds, for example "Saran" (Registered Trade Mark), is well known. Certain of our desired particles may be derived from such particles by incorporating into them by known means fuel materials such as aluminum or starch or adhering by known means to their outer surface water insoluble fuel materials such as silicon or aluminum.

In another embodiment of our invention the particles comprising fuel material may be formed from a foam. Foam particles are well known in the art and may for example be formed from inorganic materials such as glass, metals or alloys of metals but more usually from plastics materials such as for example polyurethane, polystyrene, nylon or urea formaldehyde.

In a further embodiment of our invention the polymeric particles or granules are vesciculated polymeric particles or granules comprising fuel material.

By vesciculated polymeric particles or granules we mean particles or granules of polymer, preferably spheroidal granules, which have a cell-like structure, the walls of which are provided by the polymer. The granules are not what is known in the art as foams, that is to say they are not joined together in an aggregation of cellular structures. The granules comprise a plurality of cells or vesicles, that is they are not mono-cellular or balloon-like. The vesicles are not necessarily of uniform size. Ideally such vesicles should be enclosed in a continuous shell of polymer and such granules are preferred. However it is not always easy, nor is it essential to achieve this. For example, if the granules are produced directly in the vesciculated material by e.g. by a suspension polymerisation process, there will be a random distribution of imperfect vesicles formed therein. On the other hand if the granules are prepared by, for example, the mechanical degradation of bulk vesciculated polymer, substantially all of the vesicles adjacent to the outer surface will be imperfect; that is part of the shell of the polymer which preferably encloses them will be broken away. Such imperfect vesciculated polymer granules whilst not preferred are suitable for use in composition according to our invention. Typical suitable vesciculated polymeric particles or granules are particles or granules having a mean diameter of 1 to 500 micron and the volume of the vesicles being from 5 to 95 percent of the volume of the granules and having incorporated therein or attached thereto fuel material as hereinafter defined. For certain purposes vesciculated granules of diameter as low as 0.1 micron are suitable.

In yet a further embodiment the polymeric particles or granules are retiporous polymeric particles or granules comprising fuel material. By retiporous polymeric particles or granules we mean particles or granules of
polymers wherein there is spread throughout the granule a net-like web of pores or ducts defined by the polymer comprising the granule. The individual pores are not required to be of uniform diameter nor are they necessarily of constant cross-sectional area and shape. The actual shape of the pores is imparted by the skeleton of the polymer defining them and it is characteristic of the reticulated granules that this skeleton resembles a mass of irregular, frequently rod-like, fragments of polymer linked together in a lattice-like structure. The surface of the reticulated granule may be a smooth shell of polymer; alternatively it may be pierced by randomly exposed ends of individual pores. The shell is not necessarily of uniform thickness but may comprise areas where an otherwise exposed pore is sealed by a thin membrane film of polymer. Typical reticulated particles or granules are those having a mean diameter of 1 to 500 micron and a total pore volume of the granule as measured for example by a mercury porosimeter from 10 to 60 percent of the granule volume. Such vesiculated or reticulated granules may be prepared by known means and fuel material may be incorporated therein or attached to the surface thereof by known means.

The particulate material may be particles or granules of varying shape. Thus the particles may be of irregular shapes or regular geometrical shapes for example cubes, polyhedrons, quasispheres and spheres. Exact geometrical regularity is not critical. However, because of advantages accruing from the ease of their manufacture quasispherical or spherical shaped particles are preferred. The ratio of thickness of the outer wall of the particle or granule to the diameter or overall dimension of the particle or granule is not narrowly critical. The outer wall should be of sufficient thickness to withstand fracture during transport, or during mixing or pumping operations where incorporated in our compositions. However the wall of the particle or granule should be thin enough so that it is ruptured during detonation of the composition in which it is incorporated.

The mean diameter or overall dimension of the various types of granules suitable for use in our invention is not narrowly critical. We have found that granules having a mean diameter from 0.1 to 5,000 micron or more can be used for the purposes of our invention. In general we have found that granules having a mean diameter of from 1 to 400 micron are suitable and under some circumstances, depending on the required sensitivity of the explosive compositions, granules having a mean diameter of from 1 to 100 microns may be used.

The amount of granules incorporated into our compositions depends amongst other things on the amount of gaseous matter it is desired to incorporate in the composition. This in turn is related to the diameter of the granules and the volume of the cells, vesicles or pores capable of encapsulating gas within the granule. We have found that amounts up to 15 percent w/w of the total composition may be used and that amounts from 0.5 to 10 percent w/w are suitable for most purposes.

Such particles are eminently suitable for use in our invention since they contain a gas for example oxygen, nitrogen, carbon dioxide or acetylene or a mixture of gases, for example air, in their internal structure. Because of their structure it is also possible to incorporate within the interior of the particles material suitable as a fuel in an explosive composition. Such a fuel is in close proximity to the gas or gases within the particles and this close spacial relationship between fuel and gas is exceptionally advantageous when the particles or granules are incorporated in our explosive compositions. The proximity of gas bubbles and fuel provides enhanced conditions for reaction between them. In addition desensitization of the explosive slurry by compression or loss of the air bubbles, a common phenomenon in the prior art under static pressure or during pumping is avoided or greatly reduced by their use. Furthermore by their use the sensitivity of our compositions on storage is maintained more nearly constant than is possible with prior art compositions and the presence of such particles in our compositions allows such compositions to be remixed after storage with a loss of air considerably less than has hitherto been possible.

When our particles or granules suitable for incorporation in our compositions are derived from plastics materials, the plastics materials should be water insoluble or substantially water insoluble. Typical plastics materials which may be used are for example the condensation products of polyacrylic acids with polyols or polyamines; caprolactam condensation products of the nylon 6 type; polyester amides; polyurethanes comprising the reaction products of polyls and polyols; polyethers; polyesters; epoxide and epoxyamine resins; polyamides and ionic polymers such as nylon 66 salt; polymers and copolymers of alpha, betaethylenically unsaturated monomers; resins of the condensation type, such as the condensation products of phenols, urea or amino-triazines such as melamine formaldehyde; esters of cellulose such as cellulose nitrate and cellulose acetate butyrate; chlorinated rubbers.

Fuel material may be incorporated in or attached to particles or granules suitable for use in our composition by known means. Thus in one embodiment of our invention our compositions have incorporated therein particles, for example hollow, vesiculated or reticulated particles, having deposited on the outer walls thereof a layer of a water insoluble or sparingly water soluble fuel. Such a layer may be discontinuous but it is preferred that it encompasses the outer walls substantially completely. The fuel should be in divided form preferably in finely divided form to facilitate application to the particle wall and to promote adequate adhesion between the fuel material and the walls of the particulate material. The method of applying the fuel to the particulate surface is not narrowly critical. Thus for example the particles may be treated with a water insoluble adhesive and then passed through a bed of divided fuel material, thus producing a particle coated at least in part with a layer of water insoluble or sparingly water soluble fuel. As a further example the adhesive material may be in the form of an aqueous solution when applied to the particles; the wet particles are then passed through a source of divided fuel material and the coated particle is then subjected to a further treatment, such as heating, to remove the water and to render the adhesive water insoluble. Alternatively the fuel material may be dispersed in the adhesive material and applied to the particles in one operation. The amount of fuel material applied to the surface of the particles may be controlled to any desired extent by repeating the coating operation one or more times.
In another embodiment of our invention the particu-
lar matter has incorporated within the walls or solid
portions of the particles a water insoluble or sparingly
water soluble fuel material. Thus in the preparation of
hollow particles there may be included amongst the
raw material ingredients used to prepare the particles
an amount of water insoluble or sparingly water soluble
material. Typically aluminium, magnesium or a starch
may be included in such a formulation. Such particles
may also be modified by applying to their outer surface
further suitable fuel materials by the processes herein-
before described.

In a further embodiment of our invention the parti-
cles or granules have incorporated in the hollow space
or spaces of the interior of the particles or granules fuel
material. Such fuel includes not only water insoluble or
sparsely water soluble fuels, but also water soluble
fuels. Thus for example vesicular particles may be pre-
pared wherein a water soluble fuel, for example sugar,
is located in the vesicles of the particles. Such particles
may also be modified by applying to their outer surface
further suitable fuel materials by the processes herein-
before described.

Whilst the above embodiments have described parti-
cles or granules wherein the fuel material is located on
the outside of the particle and in the vesicles, pores and
solid portions of the interior of the particle and in the
walls of the particle it lies within our invention for the
fuel material to lie within any one of any combination
of these locations. Thus for example it may be present
in the interior and the wall of the particle; in the interi-
or of the particle and attached to at least part of its
exterior surface; in the wall of the particle and attached
to at least part of its exterior surface; or in the interior
and wall of the particle and attached to at least part of
its exterior surface.

We prefer that the oxygen releasing salt be chosen
from the nitrates of the alkali or alkaline earth metals
or ammonium and of these we prefer sodium nitrate,
calcium nitrate and ammonium nitrate. The amount of
oxygen releasing salt in our compositions is not nar-
rowly critical; we have found that compositions con-
taining amounts of oxygen releasing salts from 50 per-
cent w/w to 90 percent w/w of the total composition
are satisfactory and amounts from 65 percent w/w to
85 percent w/w are preferred. The particle size and
shape of the oxygen releasing salt is not critical and is
well known from the art of ammonium nitrate manu-
facture; powders and grinded particles are satisfactory.

The oxygen releasing salts are usually in solution or
are dispersed as a slurry in our compositions. However
we have found that the sensitivity to detonation of our
compositions is enhanced if part of the oxygen releas-
ing salt component of our compositions is incorporated
or encapsulated within the interior of the water insolu-
ble particles used as a sensitizing additive. Thus when
the water insoluble particles are based on a polymeric
material, for example vesiculated polymeric materials,
the raw materials from which the particles are made
may be chosen to include an oxygen releasing salt and
the method by which the particles are made may be
performed in a manner such that oxygen releasing salt
is incorporated within the particles. Accordingly we
provide in a further embodiment of our invention ex-
plusive compositions of matter as hereinbefore de-
scribed wherein the sensitizing additive particles are
classified still further in that they comprise at least
one oxygen releasing salt.

When referring to fuels or fuel materials throughout
this specification we mean substances which are stable
in our explosive compositions, that is prior to detona-
tion, during preparation and storage the substance is
chemically inert to the system. The said substances
must be combustible and burn in the presence of a gas
and their physical nature should be such that they may
be incorporated in our compositions in a manner so as
to be uniformly distributed if desired throughout the
compositions. In addition the physical nature of the
said substances should be such that they may be incor-
porated in or attached to the particles of our composi-
tions if desired. Such fuels are well known in the art and
they may be organic or inorganic and may also be de-
formed from animals and plants.

The fuels employed in the compositions of this inven-
tion can be, for example, self-explosive fuels, non-
explosive carbonaceous, non-metallic and metallic
fuels or mixtures of the aforementioned types of fuels.
They can be varied widely. Examples of self-explosive
fuels include one or more organic nitrates, nitro com-
pounds and nitramines such as trinitrotoluene, cyclotri-
( or tetra)methylenetri (or tetra)nitramine, tetryl, pen-
terythritol tetranitrate, explosive grade nitrocellulose
and nitrostarch.

The self-explosive fuel can be for example in any of
the well known flake, crystalline or pelleted forms. In
general up to 35 percent and preferably from 10 to 30
percent by weight based on the weight of composition
of self-explosive fuel is used.

Suitable water soluble fuels are organic water soluble
substances for example urea, carbohydrates such as
sugars or molasses, water soluble alcohols or glycols,
glues or mixtures of these. The proportion of water sol-
uble fuel when present in our compositions are usually
present in an amount from 0.8 percent w/w to 8 per-
cent w/w of the total composition. Amounts from 4
percent w/w to 7 percent w/w of the total composition
are preferred.

Suitable water insoluble or sparingly water soluble
fuels may be chosen from inorganic materials for exam-
ple sulphur, aluminium, silicon, ferrosilicon, ferrophos-
phorus, magnesium, titanium, boron, mixtures thereof
for example mixtures of aluminium with ferrosilicon, or
organic materials for example finely divided charcoal,
anthracite, gilsone, asphalt, cellulose materials such as
sawdust, or cereal products for example flours, dex-
trins or starches. When the inorganic fuel is a metal it is
preferably in powder form ranging in particle size
from very fine, for example a powder passing a 325
B.S.S. sieve, to coarse, for example a powder retained
on a 30 B.S.S sieve. Such powdered metal may be in the
form of discrete regular shaped particles, but metal
powders wherein the metal is in the form of irregular
shaped particles, or in flakes or in the form of aggreg-
gates of particles or flakes are also satisfactory. The
powdered metals may be added to our compositions in
a dry form but it is also convenient to use powdered
metals dispersed in a liquid medium.

Preferred fuels are the metallic powders. The most
preferred fuel is fine aluminium, particularly paint fine
aluminium which has been treated so as to provide it
with a hydrophobic coating for example a coating of
stearic acid. Other particularly preferred fuels are the
so-called atomized metals, for example atomized alu-
mumium, which are available commercially in the form of particles which pass a 350 B.S.S. sieve. The proportion of water insoluble or sparingly water soluble non-metallic fuels when present in our compositions should be in the range from 1 percent w/w to 10 percent w/w of the total composition and amounts from 4 percent w/w to 7 percent w/w of the total composition are preferred. The proportion of metallic water insoluble fuels when present in our compositions may be as high as 25 percent w/w and amounts in the range from 0.5 percent w/w to 20 percent w/w of the total compositions are preferred.

The proportion of water in our compositions should be sufficient to dissolve at least part of the water soluble fuel when present, and part of the oxygen releasing inorganic salt say from 5 percent w/w up to 35 percent w/w but not be in excess of the explosive limit of the composition. We prefer that the water be in the range from 5 percent w/w to 25 percent w/w of the total composition and more preferably in the range from 12 percent w/w to 17 percent w/w of the total composition.

Where desirable, it is convenient to add to the compositions according to our invention, in amounts expressed as parts by weight per 100 parts by weight of the final mixture, conventional thickeners, for example, guar gum, in amounts in the range from e.g. 0 to 1 part; conventional cross-linking promoters, for example zinc chromate, in amounts in the range e.g. from 0 to 0.5 part; conventional cross-linking retardants, for example tartaric acid, in amounts ranging e.g. from 0 to 0.1 part, conventional anti-foaming agents, for example ethyl hexanol, in amounts ranging e.g. from 0 to 0.1 part, or conventional surfactants, for example non-ionic surfactants such as alkylene oxide condensates of phenols or amides, from 0 to 5 parts.

The compositions according to this invention are usually pourable and pumpable slurries or dispersions but may also be prepared as mouldable or extrudable plastic masses. They are advantageous in that they have increased and more constant sensitivity over similar explosive compositions not containing our particulate materials. Our compositions permit blasting in smaller holes down to a diameter of 1 inch less, maintain sensitivity more nearly constant during storage or after having been pumped than is possible with prior art compositions and consequently extend the useful period of storage. The increased sensitivity of our compositions also permits savings resulting from the reduction of the amount of detonating material required.

Our invention is now illustrated by but not limited to the following examples in which parts and percentages are expressed on a weight basis unless otherwise specified. Examples 11, 12 and 22 are not within our invention and are included for the purposes of comparison.

Examples 1 to 10 inclusive and 25 to 41 inclusive illustrate typical particles which are suitable for incorporation in the compositions of our invention and the method of preparing them.

**EXAMPLE 1**

In this example there is described the preparation of vesiculated polystyrene granules in which a fuel has been incorporated into the vesicles.

(A) Finely divided aluminium powder (30 parts) was efficiently dispersed in water (20 parts) in the presence of sodium hexametaphosphate (0.4 part). Sufficient water was then added to this dispersion to provide the relative volume of fuel, based on the total volume of fuel required in the final vesicle. In this case the fuel content of the vesicle was to be 10 percent by volume and the above dispersion (25.2 parts) was mixed with water (10 parts) to provide this fuel content together with 0.880 ammonia (1 part).

23 parts of 95/5 styrene/hydroxyethyl methacrylate copolymer in which each hydroxyl group has been reacted with maleic anhydride to produce a half ester, were dissolved in a mixture of azodiisobutyronitrile (1.3 parts), styrene (32 parts), and divinyl benzene (3.6 parts), and into the product was emulsified the above aqueous fuel dispersion using a high speed stirrer. The resulting emulsion was then emulsified in an aqueous phase consisting of partially hydrolysed poly-(vinyl acetate) available commercially under the Registered Trade Mark “Gelvatol” 20/90 (50 parts of 10 percent by weight solution in water), hydroxyethyl cellulose (50 parts of a 2.5 percent by weight solution in water) and water (165 parts) using a conventional stirrer. The final emulsion was be polymetrised in a closed pressure vessel heated at 90°C for three hours in a water bath. The resulting granules were washed, deanted and dried. The average granule diameter was estimated to be 12 micron and the average vesicle diometer to be 2 micron. The vesicle volume was found to be 34 percent based on the total volume of granule.

It was confirmed by the use of the scanning electron microscope that aluminium was present in the vesicles.

Repeating this process but varying the aluminium content of the vesicle, suitable adjustment of the proportion of aluminium in the initial dispersion and varying the average granule and vesicle diameters by adjustment of the rates of stirring employed, granules with the following characteristics were prepared:

<table>
<thead>
<tr>
<th>Average</th>
<th>Average</th>
<th>Vesicle</th>
<th>Aluminium</th>
</tr>
</thead>
<tbody>
<tr>
<td>granule</td>
<td>vesicle</td>
<td>volume</td>
<td>content as</td>
</tr>
<tr>
<td>diameter</td>
<td>diameter</td>
<td>%</td>
<td>% of vesicle</td>
</tr>
<tr>
<td>micron</td>
<td>micron</td>
<td></td>
<td>volume</td>
</tr>
<tr>
<td>B</td>
<td>14</td>
<td>3</td>
<td>27</td>
</tr>
<tr>
<td>C</td>
<td>15</td>
<td>3</td>
<td>23</td>
</tr>
<tr>
<td>D</td>
<td>18</td>
<td>3</td>
<td>25</td>
</tr>
<tr>
<td>E</td>
<td>15</td>
<td>3</td>
<td>22</td>
</tr>
<tr>
<td>F</td>
<td>12</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>G</td>
<td>20</td>
<td>4-5</td>
<td>16</td>
</tr>
<tr>
<td>H</td>
<td>22</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>I</td>
<td>20</td>
<td>4</td>
<td>25</td>
</tr>
</tbody>
</table>

**EXAMPLE 2**

In this example there is described the preparation of vesiculated polystyrene granules in which the polymer contains a fuel material.

(A) Aluminium powder (13.6 parts) was efficiently dispersed in a mixture of divinyl benzene (3.6 parts) and styrene (32 parts) in which had been dissolved 23 parts of the copolymer half-ester described in Example 1. Azodiisobutyronitrile (1.3 parts) was then added to the dispersion and the dispersion emulsified with water (22 parts) and 0.880 ammonia (1 part) using a high speed stirrer.

The resulting emulsion was then emulsified in an aqueous phase containing “Gelvatol” 20/90 (50 parts
of a 10 percent by weight solution in water), hydroxyethyl cellulose (50 parts of a 2.5 percent by weight solution in water) and water (165 parts) with a conventional stirrer. This emulsion was polymerised at 90°C for three hours in a closed pressure vessel.

The resulting vesiculated polystyrene granules were washed in water, decanted and then dried.

The granules contained 5 percent of aluminium by volume based on the volume of polymer in the granule and the use of the scanning electron microscope confirmed that the aluminium was present in the polymer rather than in the vesicles.

It was estimated that the average granule diameter was 22 micron and that the average vesicle diameter was 4 micron. The vesicle volume of the granules was 16 percent based on the total granule volume.

Repeating this process but using different proportions of aluminium and varying the rates of stirring employed, granules with the following characteristics were prepared.

<table>
<thead>
<tr>
<th>Example 3</th>
<th>Average vesicle volume of content</th>
<th>Average vesicle diameter</th>
<th>Aluminium content as % of polymer volume</th>
<th>Average vesicle diameter</th>
<th>Micron</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>15</td>
<td>3.4</td>
<td>20.0</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>12</td>
<td>4.0</td>
<td>15.0</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>13</td>
<td>1.6</td>
<td>7.0</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>30</td>
<td>4.0</td>
<td>19.0</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>15</td>
<td>4.0</td>
<td>20.0</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>12</td>
<td>3.4</td>
<td>19.4</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

In this example there is described the preparation of vesiculated poly(styrene) granules with a volume average diameter of about 15 micron and in which both the vesicles and the polymer contain fuel material.

A surface active agent was prepared by reacting a styrene/methacrylic acid copolymer (25.8/0.74 by weight) with 0.4 parts of a condensate of epichlorohydrin and diphenylpropane which had an epoxide equivalent of about 190 and a viscosity of 125 poise at 25°C. The agent was prepared as a 32.9 percent by weight solution in styrene which had a viscosity of 6.6 poise at 25°C.

Using a high-speed mixer, 25.0 parts of silicon particles were dispersed into a mixture of 17.5 parts of the above solution and 12.5 parts of styrene to give dispersion (a).

A suspension of 22.5 parts of silicon in a mixture of 18.9 parts of water and 3.6 parts of triethanolamine was emulsified into dispersion (a) using a high-speed mixer, to form a viscous emulsion, dispersion (b).

Dispersions (b) was added in bulk to a solution of 0.45 parts of hydroxethyl cellulose which as a 1 percent solution in water had a viscosity of about 200 poise at 25°C and 0.6 parts of an 88 percent hydrolysed grade of poly(vinyl acetate) of weight average molecular weight approximately 125,000 in 70 parts of water. The mixture was mechanically stirred at a rate which formed in 3 minutes emulsified particles of dispersion (b) having a volume average particle diameter of about 15 micron; dispersion (c).

To dispersion (c) was added 0.75 parts of azodiisobutyronitrile and the styrene polymerised by heating the charge to 70°C in a reaction vessel fitted with a stirrer and reflux condenser, for ten hours. The charge was then diluted with 2,000 parts of water and allowed to settle for two days. The sedimeted granules were separated by decantation, filtered and dried.

Microscopic examination of the granules confirmed the presence of silicon in both the polymer and the vesicles, the volume average diameter of the granules being approximately 15 micron.

It was estimated that the granules contained approximately 30 percent by volume of vesicles and that the vesicles contained of the order of 15 percent by volume of silicon. The average vesicle size was estimated by microscopic examination of dispersion (b) to be about 1 micron.

Example 4

This example describes the preparation of vesiculated methyl methacrylate copolymer granules by the dispersion of aqueous droplets in a methyl methacrylate copolymer solution and the subsequent emulsification of this dispersion into a water phase and extraction of the solvent. The vesicles contain sugar which is a water soluble fuel.

16.2 parts of an 86/14 copolymer of methyl methacrylate and dimethyl amino ethyl methacrylate quaternized with benzyl chloride, were dissolved in toluene (40 parts). The solution was added to 50 parts of a 10 percent solution of sugar in water using a high dispersion speed stirrer to produce a suspension of sugar solution droplets in the polymer solution in which the dispersed phase sugar solution particles had a maximum diameter of 5 micron.

This dispersion was emulsified in an aqueous phase consisting of “Gelvalot” 20/90 (11 parts of a 13.6 percent solution in water), hydroxyethyl cellulose (55 parts of a 2.25 percent solution in water) and a 10 percent solution of sugar in water (133 parts) using a conventional stirrer. The emulsified particles of sugar-containing polymer solution were of average diameter approximately 35 micron. The toluene was extracted from the particles by stirring the emulsion with an aliphatic hydrocarbon (500 parts) and the resulting vesiculated polymer granules diluted with water (4,000 parts) recovered by decantation and dried. Porosity measurements indicated that the granules had a vesicle volume of about 60 percent of the total volume of the granules. The maximum diameter of the vesicles was 4 micron and the average granule diameter was approximately 25 micron. The presence of sugar in the granule was confirmed analytically.

Example 5

Preparation of vesiculated granules of poly(styrene/divinyl benzene) in which the vesicles comprise a proportion of fuel particles.

A copolymer of glycylid methacrylate/vinyl pyrrolidone (3/97 mol. ratio) was prepared using ethylene glycol monomethyl ether as a solvent. This copolymer was reacted with sufficient methacrylic acid to introduce approximately one polymerisable double bond per polymer chain. Finally the modified copolymer was copolymerised with styrene to form essentially a branched poly(vinyl pyrrolidone)/poly(styrene) copolymer solution.

Pigment grade aluminium was then dispersed in this polymer solution and styrene added causing the poly(vinyl pyrrolidone) chains of the copolymer to collapse
around the aluminium particles which, however, remained in a state of stable dispersion. To 90 parts of the above dispersion, which contained 10 parts of aluminium and 5 parts of vinyl pyrolidone copolymer was added 5.6 parts of divinyl benzene and 2 parts of azodisobutyronitrile. This mixture was emulsified into an aqueous suspending liquid, consisting of 50 parts of a 10 percent by weight solution in water of poly(vinyl alcohol), 50 parts of a 2.5 percent by weight solution in water of hydroxy ethyl cellulose and 165 parts of water, using a high speed stirrer. The vinyl pyrolidone copolymer particles were swollen by water imbibt from the suspending liquid. Polymerisation of the medium was carried out by heating the batch to 90°C in a closed vessel for three hours. The granules so formed were washed with water, collected by decanting and dried.

The average diameter of the dried granules was 5 micron, the vesicle volume 20 percent of the granule volume and the diameter of the vesicles approximately 1.5 micron. Scanning electron micrograph examination of the granules confirmed the presence of aluminium particles within the vesicles.

EXAMPLE 6
An unsaturated polyester resin was prepared by conventional means from propylene glycol (30.0 parts), maleic anhydride (26.7 parts) and phthalic anhydride (13.5 parts). The product had an acid value of 40 mgm KOH per gram and a Gardner Holdt viscosity of Z3 as a 70 percent by weight solution in ethyl cellosolve. A solution of 26.8 parts of the unsaturated polyester resin and 1.5 parts of benzyol peroxide in 26.8 parts of styrene having dispersed therein 32.9 parts of finely divided aluminium powder was added with high speed stirring to an aqueous liquid consisting of 0.35 part of hydroxy ethyl cellulose, 0.7 part of "Gelvatol" 20/90 and 99.3 parts of water. The mixture was stirred for one hour and there was then added 1.7 parts of diethylene triamine and 1.4 parts of ammonia. Whilst maintaining stirring the temperature was raised to 60°C and maintained at this temperature for one hour. Vesiculated granules were formed and the suspension of granules so obtained was diluted with 600 parts of water, allowed to stand for a day and the concentrated suspension of sedimented granules separated from the bulk of the water. The granule diameter ranged from 10 to 100 microns and it was estimated by microscopic examination that the granules comprised about 30 percent by volume of vesicles. The vesicles had diameters mainly ranging from 2 to 20 microns with a few of the larger particles having vesicles of about 50 microns diameter. On allowing the granules to dry in air substantially air filled vesicles were formed. The granules contained 37.8 percent aluminium which was dispersed mainly in the body of the polymeric granule. Some of the aluminium was present in some of the vesicles and a further small amount of aluminium was embedded in the polymers forming the walls of the granules.

EXAMPLE 7
7 parts of a 70/30 copolymer of methyl methacrylate and ethyl acrylate were dissolved in 34 parts of methyl ethyl ketone. 10 parts of paint fine aluminium were dispersed in the solution so formed. To the dispersion of aluminium was added 10 parts of the vesiculated granules described in Example 6. The suspension of vesiculated granules was stirred gently at room temperature whilst the methyl ethyl ketone evaporated spontaneously. The resultant product comprised vesiculated granules with a layer of aluminium adhered to their outer surface by means of the water insoluble copolymeric adhesive.

EXAMPLE 8
The general procedure of Example 7 was repeated but the vesicated beads of that example were replaced by 10 parts of retiporous granules of melamine/formaldehyde resin wherein the formaldehyde/melamine molar ratio was 4:1. The granules were of 15 micron average diameter and with a porosity of about 18 percent by volume. The resultant product comprised retiporous granules with a layer of aluminium adhered to their outer surface by means of the water insoluble copolymeric adhesive.

EXAMPLE 9
The general procedure of Example 7 was repeated but the vesiculated beads of that example were replaced by 20 parts of monomolecular glass spheres of average diameter 50 microns. The resultant product comprised inorganic monomolecular particles with a layer of aluminium adhered to their outer surface.

EXAMPLE 10
In this example is described the preparation of vesiculated polystyrene aluminium containing granules by the emulsification of water droplets in styrene in the presence of a stabiliser, and the subsequent emulsion polymerisation of the styrene in an aqueous phase. Finely divided aluminium powder (30 parts) was efficiently dispersed in water (20 parts) in the presence of sodium hexametaphosphate (0.4 part). 25.2 parts of this dispersion were mixed with water (10 parts) and 0.880 ammonia (1 part). A latex of a 95/5 styrene/dimethylamino-ethylmethacrylate (DMAEM) copolymer quaternised with benzyl chloride (10.4 parts) in water (51 parts) stabilised with cetyl trimethyl ammonium bromide (0.53 parts) was mixed, using a high speed stirrer, with styrene (32 parts), divinyl benzene (3.6 parts), azo disobutryronitrile (1.3 parts), sorbitan monostearate (3.0 parts). Into this product was emulsified the above aqueous fuel dispersion using a high speed stirrer and the whole mixture was then emulsified in an aqueous phase consisting of partially hydrolysed poly(vinyl acetate) "Gelvatol" 20/90 (50 parts of a 10 percent by weight solution in water), hydroxy ethyl cellulose (50 parts of a 2.5 percent by weight solution in water) and water (165 parts) using a conventional stirrer so as to avoid breakdown of the water in monomer dispersion. The emulsified particles of water-containing monomer were of diameter approximately 15 micron. The emulsion was heated in a closed pressure vessel at 90°C for three hours in a water bath to polymerise the particles of monomer. The resulting vesiculated polymer granules were added to water (4.5 parts), agitated and then allowed to settle to be recovered by decantation and drying. Porosity measurements indicated that each granule had a vesicle volume of 21 percent of the total volume of the granule. It was confirmed that the average diameter of the granules and the average diameter of the vesicles were substantially the same as the average diameters of the emulsified monomer in water particles and disperse water.
particles respectively. It was confirmed by microscopy that aluminium was present in the vesicles.

The granule diameter may be varied by varying the rate of stirring. At lower rates of stirring granules of diameter up to 500 micron were obtained with vesicle size 2 - 3 micron. The larger size granules contained a higher volume of vesicles, up to 60 percent by volume in the case of granules of diameter 500 micron. At higher rates of stirring the granule size was reduced to about 5 micron with a corresponding reduction in vesicle size. The volume of vesicles in the granules may also be varied by varying the proportion of water dispersed in the monomer.

EXAMPLE 11

For comparative purposes a composition not according to our invention consisting of ammonium nitrate prills 68.4 parts; sodium nitrate 2.5 parts; sugar 5.0 parts; aluminium powder 9.0 parts; silicon 1 part; water 13.0 parts; guar gum 0.5 part; zinc chromate 0.1 part and tartaric acid 0.01 part was prepared. A portion of this composition was compounded in 4 inch diameter cardboard cylinders. The minimum amount of pentolite required to detonate a cartridge so prepared was 250 g. Another portion of this composition was pumped through a "Mono" pump prior to cartridging in cardboard cylinders (“Mono” is a registered trade mark. This pump is of the positive displacement type fitted with a screw feed). Using 250 g of pentolite as a detonating material no detonation of the pumped composition could be obtained in a cardboard cartridge of 4 inches diameter, nor even in a cardboard cartridge of 5 inches diameter, i.e., under less stringent conditions. This example demonstrates that this comparative composition is less sensitive to detonation after pumping.

EXAMPLE 12

A composition not according to our invention consisting of ammonium nitrate 76.3 parts; glycol 5.0 40 parts; paint fine aluminium 2.0 parts; water 16.0 parts; guar gum 0.6 part and zinc chromate 0.1 part was prepared. A portion of this composition was cartridged in 1 inch diameter cardboard cylinders and was detonated by 3 X No. 8 A1 detonators. Another portion of this 45 composition was pumped through a “Mono” pump prior to cartridging in cardboard cylinders. Using 3 X No. 8 A1 detonators as the detonating means no detonation was achieved using 1 inch diameter cardboard cylinders; however, detonation was achieved using 2 inch diameter cardboard cylinders. This example demonstrates that this comparative composition is less sensitive to detonation after pumping.

13

14

3,837,937

EXAMPLES 13 to 22 INCLUSIVE

Using a mixer of the Schraeder type having a capacity of 20 lb a blasting explosive was prepared by mixing the substances set out in Table I in proportions set out in Table I. Details of the detonation conditions whereby the compositions contained in cardboard cylinders were detonated are also set out in Table I.

NOTES ON TABLE I

1. The prilled ammonium nitrate was coated with a small amount of china clay.

2. The fine ammonium nitrate was in the form of a powder, 100 percent passing a No. 6 B.S.S. sieve, 51 percent passing a No. 36 B.S.S. sieve and 18 percent passing a No. 100 B.S.S. sieve.

3. The sodium nitrate was in the form of a coarse powder.

4. The molasses contained 20 percent of water.

5. The aluminium powder passed a No. 25 B.S.S. sieve, not less than 70 percent was retained on a No. 100 B.S.S. sieve and not less than 95 percent was retained on a No. 300 B.S.S. sieve.

6. The fine aluminium powder was of the type conventionally used for the purposes of pigmentation and had been coated so as to have a hydrophobic surface.

7. The silicon was in the form of a powder, 95 percent passing a No. 30 B.S.S. sieve, 90 percent passing a No. 100 B.S.S. sieve.

---

**TABLE I**

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TABLE I – Continued

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<tr>
<td>Minimum pentolite required to detonate (g)</td>
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</table>

EXAMPLE 23

The composition of Example 20 was pumped through a "Mono" pump prior to cartridgeing in 3 inch diameter cylinders. Detonation of the pumped cartridge composition was achieved using 50 g of pentolite. The compositions of Examples 13 to 19 inclusive and 21 were pumped in a similar manner and then cartridge as set out in Table I. These pumped compositions were then detonated. In all instances the sensitivity of these compositions was found not to have been impaired by the pumping process.

EXAMPLE 24

The composition of Example 21 was stored for seven days at ambient temperature. After this time it was detonated successfully under the conditions shown in Table I in Example 21. By contrast the composition of Example 22 — not according to our invention — under the same storage conditions, could not be detonated under the conditions shown in Table I in Example 22. This example demonstrates that the addition of the granules reduced the variation in the sensitivity of the explosive composition on prolonged storage.

EXAMPLE 25

A solution of 26.8 parts of the unsaturated polyester resin prepared by conventional means from propylene glycol, maleic anhydride and phthalic anhydride as in Example 6 and 1.5 parts of benzoin peroxide in 26.8 parts of styrene having dispersed therein 35.4 parts of paint fine aluminium was added with high speed stirring to an aqueous liquid consisting of 0.35 part of hydroxyethylcellulose, 0.7 part of "Gelvatol" 20/90 1.7 parts of diethyleneimine, 1.4 parts of 0.88 ammonia and 99.3 parts of water. After stirring for 5 minutes a further 400 parts of water were added and the stirring speed was reduced. The temperature of the mixture was raised to 60°C and the stirred mixture was maintained at this temperature for a further 2 hours during which time granules were formed. The granules were collected from the suspension by filtration and were dried to give vesiculated granules of diameter in the range from 5 to 100 microns, containing airfilled vesicles of diameter in the range from 1 to 20 microns. By means of microphotographs of the granules it was estimated that the vesicles occupied approximately 40 percent by volume of the granules and that aluminium was dispersed mainly in the body and walls of the granules. The aluminium content of the particles was 33 percent.

EXAMPLE 26

The general procedure of Example 25 was repeated except that the amount of polyester resin was reduced to 7 parts, the amount of styrene was increased to 33 parts and the amount of paint fine aluminium was increased to 50 parts. There was thus obtained vesiculated particles of a styrene-unsaturated polyester resin in which the particles had a diameter in the range from 5 to 25 microns, the vesicles therein had a diameter in the range from 1 to 3 microns and occupied approximately 20 percent of the particle volume. The aluminium content of the particles was 55 percent and the aluminium was dispersed mainly in the body and walls of the particles.

EXAMPLE 27

An aqueous paste was prepared by stirring together for 5 minutes a mixture of 150 parts of Standard Lining aluminium powder No. 408 (a paint fine aluminium powder having a hydrophobic coating and substantially passing a 325 mesh sieve and which is available from Alcoa Australia Ltd. of Melbourne, Australia), 1 part of "Teric" N5 (an alkylene oxide condensate of nonyl phenol), 1 part of "Teric" 160 (an alkylaryl polyoxyalkylene ether) ("Teric" is a Registered Trade Mark of ICI Australia Ltd.), 100 parts of water and 5 parts of 0.88 ammonia. The paste so formed was dispersed with high speed mixing into a solution consisting of 100 parts of the polyester resin prepared in Example 6, 100 parts of styrene and 7 parts of benzoin peroxide. The dispersion so formed was in turn dispersed with high speed stirring in an aqueous phase consisting of 1.75 parts of hydroxyethyl cellulose, 2.1 parts of "Gelvatol" 20/90, 0.8 parts of diethylene triamine, 7 parts of 0.88 ammonia and 500 parts of water. Stirring was continued for a further 5 minutes, 400 parts of water were then added and the stirring speed was reduced. From this mixture there was obtained, using the heating and recovery procedures as described in Example 25, dry vesiculated particles of a styrene-unsaturated polyester containing 42.8 percent of aluminium most of which was located in the vesicles of the particles. The particles had diameters in the range from 5 to 100 microns; the vesicles had diameters in the range from 1 to 10 microns and occupied approximately 25 percent of the volume of the particle.

EXAMPLE 28

An aqueous paste was prepared by stirring together for 5 minutes a mixture of 120 parts of atomized aluminium powder, 1 part of "Teric" N 5, 1 part of "Teric" 160, 80 parts of fine ammonium nitrate, 1.5 parts of 0.88 ammonia, 0.2 part of diethylene triamine and 100 parts of water. This aqueous paste was dispersed into a solution consisting of 100 parts of the polyester resin prepared in Example 6, 100 parts of styrene and 7 parts of benzoin peroxide. The dispersion so
formed was in turn dispersed with high speed stirring in an aqueous phase consisting of 1.75 parts of hydroxyethyl cellulose, 32.1 parts of "Gelvalol" 20/90, 0.8 part of diethylene diamine, 7 parts of 0.88 ammonia, 400 parts of ammonium nitrate and 500 parts of water. Stirring was continued for a further 5 minutes, 800 parts of water were then added and the stirring speed was reduced. From this mixture there was obtained, using the heating and recovery procedures as described in Example 25, dry vesiculated particles having incorporated in the vesicles thereof a mixture of ammonium nitrate and aluminium. The amount of ammonium nitrate in the particles was about 21 percent of the total weight of particles and the amount of aluminium formed approximately 30 percent of the total weight of the particles.

**EXAMPLE 29**

The procedure of Example 25 was repeated except that the 35.4 parts of paint fine aluminium of that Example was replaced by 35.4 parts of atomized aluminium passing a 350 mesh sieve and available from Comalco Ltd. of Melbourne, Australia under the name of "Atomized aluminium powder 350/dust." There were thus obtained vesiculated granules containing 38.4 percent of aluminium dispersed mainly in the body and walls of the granules.

**EXAMPLE 30**

The procedure of Example 29 was repeated except that the amount of atomized aluminium was increased from 35.4 parts to 114 parts. There was thus obtained vesiculated granules containing 68 percent of aluminium located mainly in the body and walls of the granules.

**EXAMPLE 31**

The general procedure of Example 27 was repeated but the aqueous paste of that Example was replaced by an aqueous dispersion formed by stirring together 150 parts of water, 300 parts of atomized aluminium powder 350/dust, and 2 parts of "Tamol" 731 ("Tamol" 731 is a Registered Trade mark of Rohm and Haas Co. for an ionic copolymer of disobutylene and maleic anhydride). There were thus obtained vesiculated particles wherein the vesicles comprised approximately 35 percent of the volume of the particles and the particles contained 60 percent of aluminium located mainly in the vesicles of the particles.

**EXAMPLE 32**

The general procedure of Example 31 was repeated except that the 300 parts of atomized aluminium in the aqueous dispersion of that Example was increased to 330 parts. There were thus obtained vesiculated particles wherein the vesicles comprised approximately 29 percent of the volume of the particles and the particles contained 64.5 percent of aluminium located mainly in the vesicles of the particles.

**EXAMPLE 33**

The general procedure of Example 31 was repeated except that the 300 part of atomized aluminium in the aqueous dispersion of that Example was increased to 370 parts. There were thus obtained vesiculated particles wherein the vesicles comprised approximately 44 percent of the volume of the particles and the particles contained 73.7 percent of aluminium located mainly in the vesicles of the particles.

**EXAMPLE 34**

An aqueous dispersion was prepared by stirring together for 5 minutes a mixture of 240 parts of atomized aluminium powder, 95 parts of water and 1 part of "Tamol" 731. The dispser so produced was mixed with high speed stirring into a slurry which consisted of 130 parts of the polyester resin prepared in Example 6, 100 parts of styrene, 6 parts of benzoxy peroxide and 450 parts of atomized aluminium powder. The resultant mixture was dispersed with high speed stirring into an aqueous phase consisting of 1.75 parts of hydroxyethyl cellulose, 2.1 parts of "Gelvalol" 20/90, 0.8 part of diethylene triamine, 7 parts of 0.88 ammonia and 50 parts of water. Stirring was continued for 5 minutes, 400 parts of water were added, after which the stirring speed was reduced. Using the heating and recovery procedures as described in Example 25 there were recovered from the above mixture dry vesiculated granules containing 75.5 percent of aluminium of which approximately two-thirds was located in the body of the granules and one-third was located in the vesicles of the granules.

**EXAMPLE 35**

This example describes the preparation of particles of a polyurethane foam in which paint fine aluminium was located in the walls and the ribs of the air cells of the foam. A dispersion was prepared by dispersing 477 parts of aluminium powder No. 408 in 460 parts of "Suprasec" DN ("Suprasec" DN is a Registered Trade Mark of Imperial Chemical Industries Ltd. for a disocyanatodiphenylmethane). This dispersion was added quickly to a solution of 239 parts of "Daltolac" 60 ("Daltolac" 60 is a Registered Trade Mark of Imperial Chemical Industries Ltd. for an alkylene oxylated triol), 4.77 parts of water and 4.77 parts of Catalyst SFC (Catalyst SFC is a Registered Trade Mark of Imperial Chemical Industries Ltd. for a tertiary amine catalyst). The mixture was stirred vigorously for 20 minutes and poured into a simple mould. The mixture foam as the components reacted exothermally to produce a multiphase product consisting of a dispersion of gas, substantially air, and aluminium in a matrix of polyurethane. The aluminium was located predominately in the polyurethane and formed about 40 percent of the product. The product when cooled was comminuted to particles in the size range of from 100 to 4,000 microns.

**EXAMPLE 36**

A mixture of 20 parts of paint fine aluminium, 30 parts of vesiculated polyester granules prepared by the method as described in Example 13 of our copending Australian Patent application PA 3506/70, 10 parts of a copolymer of 2-ethylhexylacrylate, dimethylaminoethyl methacrylate quaternized with benzy1 chloride, and glycidylmethacrylate wherein the components are in the molar ratio 6:1:1, and 290 parts of tolutene was ball milled for 16 hours in the presence of 1,500 parts of balls of % diameter. The balls were then separated from the mixture by filtration and solvent was evaporated from the filtered slurry to give a product which was then broken down to small aggregates and granules of vesiculated granules having a coating of aluminium adhering to their outer surface. The aluminium formed 33 percent of the total weight of the coated granules.
The procedure of Example 36 was repeated but the vesiculated polyester granules of that Example were replaced by 30 parts of foamed “Saran” microspheres obtained from Dow Chemical Co. of USA under the designation XD 4519/01. The spheres had a specific gravity of 0.2 and were of diameter in the range from 20 to 30 microns. There was thus obtained microspherical particles of plastic material coated with aluminium on their outer surface and wherein the aluminium formed 30 percent of the total weight of the particles.

EXAMPLE 38

The procedure of Example 37 was repeated but the “Saran” microspheres of that Example were replaced by 30 parts of “Saran” microspheres designated by Dow Chemical Co. as XD 4519/04. These spheres were similar to those designated XD 4519/01 but were stated by the suppliers as having been surface treated. There was thus obtained microspherical particles of plastic materials coated with aluminium on their outer surface and wherein the aluminium formed 32 percent of the total weight of the coated particles.

EXAMPLE 39

The procedure of Example 36 was repeated but the vesiculated particles of that Example were replaced by 30 parts of glass balloons of particle density 0.33 g/cc and of particle size such that 90 percent of the particles had a diameter in the range from 20 to 80 microns. The balloons were supplied by Minnesota Mining & Manufacturing Company of St. Paul, Minnesota, USA under the designation B 35 D. The paint fine aluminium of Example 36 was replaced by 20 parts of silicon powder 90 percent of which passed a 100 mesh sieve. There was thus obtained glass balloons coated with silicon powder on their outer surface and wherein silicon formed 28 percent of the total weight of the coated balloons.

### TABLE II

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<tr>
<td>Velocity of detonation (m/sec)</td>
<td>3030 2800 2630 — — — — —</td>
</tr>
</tbody>
</table>

The symbol - in the Tables indicates either that a particular ingredient was not used or the test was not performed.

EXAMPLE 40

The procedure of Example 39 was repeated but the glass balloons of that Example were replaced by similar glass balloons from the same supplier but designated B 40 D and having a particle density of 0.37 g/cc. The silicon of Example 39 was replaced by 20 parts of “atomized aluminium powder 350/dust.” There was thus obtained glass balloons coated with aluminium on their outer surface and wherein aluminium formed 28 percent of the total weight of the coated balloons.

EXAMPLE 41

The procedure of Example 36 was repeated but the vesiculated particles of that Example were replaced by 30 parts of vesiculated granules prepared as described in Example 6. There was thus obtained aluminium coated vesiculated granules wherein a further amount of aluminium was located internally within the granules.

EXAMPLES 42 to 50 INCLUSIVE

Using the proportions of ingredients set out in Table II 10 lbs. of nine explosive compositions were prepared by the following general method. To a solution prepared by dissolving the fine ammonium nitrate in 10 parts of water there was added a solution prepared by mixing the guar gum and diethylene glycol. The mixture was stirred for 3 minutes after which time the zinc chromate was added followed by the addition with stirring of a mixture prepared from 6 parts of water, the particulate sensitizing additive and, when used, 0.1 part of an alkylene oxide condensate of coconut monothanolamide available commercially under the Registered Trade Mark “Teric” CME3. The resultant mixture was stirred for 3 minutes and then stored for 16 hours after which time portions of each composition were packaged in cardboard cylinders and detonated under the conditions set out in Table II. A further portion of each composition was pumped through a “Mono” pump prior to being packaged in cylinders as set out in Table II. When the pumped compositions were detonated, in no instance was it found that the sensitivity of the composition to detonation had been impaired.

We claim:

1. An explosive composition of matter comprising firstly at least one oxygen releasing salt selected from the group consisting of ammonium nitrate, chlorate
and perchlorate, alkali metal nitrates, chlorates and perchlorates, and alkaline earth metal nitrates, chlorates and perchlorates present in an amount from 50 parts to 90 parts; secondly, at least one fuel selected from the group consisting of water soluble fuel present in an amount from 0.8 to 8 parts, non-metallic sparingly water soluble and non-metallic water insoluble fuel present in an amount from 1 to 10 parts, and metallic water insoluble fuel present in an amount from 0.5 to 20 parts; thirdly, water present in an amount from 5 to 35 parts; and fourthly, as a sensitizing additive water insoluble particles present in an amount from 0.5 to 10 parts, said particles being characterized in that said particles comprise firstly a carrier component capable of encapsulating gaseous material, secondly a gaseous component encapsulated within the interior of said carrier component, and thirdly a fuel component which may be located either on the surface of said carrier component or within the interior of said carrier component or both, and wherein said fuel component constitutes up to 80 percent w/w of the weight of said particles, and wherein said particles are characterized further in that at least a part of said gaseous component is capable of reacting with said fuel component, all amounts being in parts by weight per 100 parts by weight of the composition.

2. A composition of matter according to claim 1 wherein the oxygen releasing salt is selected from the group consisting of the nitrates of sodium and ammonium.

3. A composition of matter according to claim 1 wherein the oxygen releasing salt constitutes from 65 percent w/w to 85 percent w/w of the total composition.

4. A composition of matter according to claim 1 wherein fuel is selected from the group consisting of:
   a. water soluble fuel
   b. non-metallic sparingly water soluble fuel and
   c. non-metallic water insoluble fuel or mixtures thereof and wherein any one of said fuels (a), (b) or (c) constitutes from 4 percent w/w to 7 percent w/w of the total composition.

5. A composition of matter according to claim 1 wherein water constitutes from 12 percent w/w to 17 percent w/w of the total composition.

6. A composition of matter according to claim 1 wherein the water insoluble particles present as a sensitizing additive constitute from 2 percent w/w to 6 percent w/w of the total composition.

7. A composition of matter according to claim 1 wherein the water insoluble particles used as the sensitizing additive comprise material selected from the group consisting of vesiculated, reticulous and foamed polymeric or copolymeric plastic particulate materials.

8. A composition of matter according to claim 1 wherein the water insoluble particles used as the sensitizing additive are hollow, monocular or balloon like particles comprising polymeric or copolymeric plastic materials or glass.

9. A composition of matter according to claim 1 wherein the water insoluble particles used as the sensitizing additive are characterized still further in that they comprise at least one oxygen releasing salt.

10. A composition of matter according to claim 9 wherein the oxygen releasing salt in the particulate sensitizing additive constitutes up to 25 percent w/w of the weight of the said particulate additive.