

3,201,291

DISPERSION-TYPE BLASTING EXPLOSIVES

Albert Schmidt, Freiburg, Germany, assignor to
Fritz Frutiger, Beatenbuch, Switzerland

No Drawing. Filed May 29, 1962, Ser. No. 198,458
Claims priority, application Switzerland, Nov. 27, 1958,
66,728; June 25, 1959, 74,922; May 29, 1961, 6,251/61
14 Claims. (Cl. 149—22)

The present invention is a continuation-in-part of my
copending United States patent application Ser. No. 10
854,255, filed November 20, 1959.

This invention relates to explosive compositions and
refers more particularly to dispersion-type blasting ex-
plosive compositions.

Recent developments in the art of blasting explosives 15
have shown that dispersion-type blasting explosives offer
several advantages over other types of prior art blasting
explosives.

The term "dispersion-type blasting explosive composi- 20
tion" as used in the present specification and in the ap-
pendant claims is intended to designate a group of blast-
ing explosive compositions containing a substantial
amount of water, e.g. about 1 to about 30% by weight
of the total composition. The water-soluble solid or liq- 25
uid components of this type of explosive composition are
partly or completely dissolved in the amount of water
present in the composition, depending upon the solubili-
ty of the particular component at ambient temperature
in water and the entire amount of that water-soluble com- 30
ponent present in the composition. It is evident that a
composition of this type with a given water content may
contain a water-soluble component in a dissolved state
as well as in an undissolved, e.g. solid, state. Accord- 35
ingly, a composition of this type comprises an aqueous phase,
i.e. an aqueous solution of its water-soluble components.
This aqueous phase or solution usually but not neces-
sarily is the continuous phase in which the solid and/or
liquid water immiscible components of the composition are 40
dispersed. The solid components may include solid or-
ganic explosives, oxygen carriers, etc.

One well known blasting explosive composition of the
dispersion-type is a slurry of ammonium nitrate and
trinitrotoluene in water. However, such slurries require
a booster charge or relay for ignition and have a marked
tendency to settle, i.e. to become separated into sediment 45
and supernatant liquid. Furthermore, this type of blast-
ing explosive composition, as a rule, is not oxygen bal-
anced due to the relatively large amount of trinitrotoluene
necessary in this composition to ensure detonability.

Another prior art safety explosive composition of the
dispersion-type contains a high proportion (20-45%) of
high explosive ingredients, i.e. having a detonating veloc- 50
ity of above 7500 meters per second. While this composi-
tion can be ignited by means of standard blasting caps
and supplies all of the oxygen necessary for combustion
of its components (oxygen balanced composition), it is
evident that the large amount of high velocity explosive
present in this composition is disadvantageous for econ- 55
omic reasons as well as for the hazardous nature in-
volved in the use of high velocity explosives.

At present, no dispersion-type blasting explosive is
known which, at the same time, has a balanced oxygen
content, can be ignited with standard blasting caps (i.e. a
cap-sensitive composition; ignition without booster), con- 65
tains no liquid esters of nitric acid and little (up to 15%
by weight) or no high velocity explosive and which has a
brisance similar to that of the prior art nitroglycerin-
containing blasting explosives. It is evident that a blast-
ing explosive composition with the above properties would 70
be extremely desirable.

It is a primary object of the present invention to pro-
vide for an improved dispersion-type blasting explosive
composition having a balanced or compensated oxygen
content, i.e. providing at least that amount of oxygen
which is required for total combustion of the components
of the composition. It is also an important object of
this invention to provide for a blasting explosive composi-
tion which is free from liquid esters of nitric acid, such
as nitroglycerin.

A further object of the invention is a cap-sensitive dis-
persion-type blasting explosive containing a maximum of
15% by weight of high velocity explosives, if any.

Another object of the present invention is a dispersion-
type blasting explosive in a plastic or liquid form which
does not segregate or form a sediment even after pro-
longed periods of storage.

It is a further object of the present invention to provide
for an aqueous phase which when added to a particulate
solid mixture of combustible material and oxygen carrier
increases the amount of oxygen available for combustion
in such mixture, and, at the same time, transforms the
solid mixture into a plastic or liquid state.

It is still a further object of the present invention to
provide for a dispersion-type blasting explosive composi-
tion which can be ignited directly by means of a standard
blasting cap, even though it contains an appreciable
amount of water and little if any high velocity type ex-
plosive.

It is another object of the present invention to provide
for nitroglycerin-free dispersion-type blasting explosive
compositions having a brisance similar to that of known
explosive compositions containing nitroglycerin.

These and still further objects will become apparent
from the description given hereinafter.

I have now found that the above objects may be
achieved by a dispersion-type blasting explosive composi-
tion which comprises, according to an important aspect
of the invention, a combustible material dispersed in an
aqueous phase having a positive oxygen balance.

Heretofore, the aqueous phase has been used merely as
a plastizing or liquefying agent for the solid particulate
material present in dispersion-type blasting explosive
compositions. The potential advantage of using the aque-
ous phase as an oxygen source has not been realized and
in many of the prior art blasting explosive compositions
of the dispersion-type the aqueous phase had a negative
oxygen balance and a desensitizing effect upon the entire
composition. It is quite surprising that oxygen carriers
present in dissolved form, i.e. dissolved in the water
present, contribute to the oxygen balance of the composi- 50
tion and, at the same time, provide a means to in-
crease the sensitivity to ignition of a given composition.

I have found that, in general, the oxygen balance of
the aqueous phase should at least have a positive value
of 10%, preferably an oxygen surplus of from about
15 to about 25% or even more. If according to a pre-
ferred embodiment of the invention the dispersion-type
blasting explosive composition contains a major amount
of solid ammonium nitrate as oxygen carrier, it is ad-
vantageous to use an aqueous phase having an oxygen
surplus which is about equal to or higher than the oxygen
surplus of solid ammonium nitrate (+19.988%).

The terms "oxygen balance," "oxygen surplus," and
"oxygen deficiency" are well understood in the art of
explosives. For complete combustion of a given sub-
stance a certain amount of oxygen is necessary which
may be easily calculated from the chemical formula of
the combustible substance. Since detonation is a rapid
combustion the same considerations are applicable.
Accordingly, an oxygen deficient substance or composi-
tion needs oxygen for its combustion, whereas a sub-
stance or composition with an oxygen surplus supplies

more oxygen during its combustion or decomposition as is necessary for complete oxidation of all its components. In this latter case, free oxygen will usually be among the products of combustion. It should be noted that, for example, oxidation of carbon is regarded as complete only then if the product of combustion contains substantially only carbon dioxide, or a molar mixture of carbon monoxide and oxygen. A substance or composition having a balanced oxygen content supplies substantially the entire amount of oxygen necessary for complete combustion of its components.

From the above explanation it is evident that an oxygen deficient blasting explosive composition is undesirable for two reasons; some of the products of incomplete oxidation are highly toxic, such as carbon monoxide and some nitrogen oxides, and if such products are used in closed areas, such as tunnels or mines, the atmosphere becomes contaminated with toxic components.

On the other hand, the products of incomplete combustion represent a loss of energy, i.e. a lower energy yield from a given explosive. A further hazard results from uncontrolled oxidation or ignition of the products of incomplete oxidation.

Accordingly, for reasons of safety as well as economy, it is highly undesirable to employ explosive compositions which are oxygen deficient. The dispersion-type blasting explosive compositions according to the invention supply at least as much oxygen as is necessary for the total oxidation of its components. The composition of the invention preferably has a balanced oxygen content and may have a certain oxygen surplus. Such surplus, however, should not exceed about 8% and preferably should be below about 5% by weight, i.e. the oxygen balance of the dispersion-type explosive compositions of the invention is in the range from 0 to +8% and preferably from 0 to about 5% by weight.

The calculation of the oxygen balance of a composition is a basic and well known operation in the art. For convenience, standard tables are used which give the oxygen numbers for various substances commonly employed in explosive compositions. An "oxygen number" is the oxygen balance of 100 grams of a given substance and may have a positive or negative value, or is zero. Tables with such oxygen numbers are to be found in the book by Dr. Alfred Stettbacher, entitled "Spreng- und Schiesstoffe," Rascher Verlag, Zurich, Switzerland, 1948, on pages 170-175.

In order to calculate the oxygen balance of a given composition the oxygen number of each component is multiplied by the percentual (weight) amount in which each component is present in the composition. The result is the oxygen number of the composition which number again may have a positive or negative value, or is zero. This number is identical with the percentual (weight) amount of the oxygen balance.

In my publication in "Nobel Hefte, Sprengmittel in Forschung und Praxis," 1961, 1, pages 1-9, examples for the calculation of the oxygen balance, heat of explosion, and gas volume of explosive compositions are given.

If, for example, an oxygen balanced mixture of trinitrotoluene (TNT) and sodium nitrate (SN) is to be prepared it may be calculated as follows:

Oxygen balance of TNT: -73.97

Oxygen balance of SN: +47.04

$(73.97 + 47.04) : 73.97 = 100 : X_{SN}$

$X_{SN} = 61.12\% \text{ SN}$

$73.97 : 47.04 = 100 : X_{TNT}$

$X_{TNT} = 38.88\% \text{ TNT}$

A mixture of 61.12% by weight of sodium nitrate and 38.88% by weight of TNT has a balanced oxygen content.

Only very few explosive substances have a positive oxygen balance per se. Nitroglycerin, for example, has

an oxygen balance of +3.523. The use of nitroglycerin and other normally liquid esters of nitric acid is expressly excluded for compositions according to the present invention, in view of the hazardous properties of these substances.

Pentaerythritol-tetranitrate (PETN) and some other normally solid esters of nitric acid or explosive substances of a different type, e.g. nitramines, such as tetryl, having a detonating velocity (standard value) of above 7500 meters per second may be used for compositions according to the present invention in an amount of up to 15% by weight of the entire composition. Their use in an amount of more than 15% is not preferred due to the high costs and some hazards involved if compositions with a major amount (i.e. more than 15%) of PETN or similar substances are to be prepared and used.

The dispersion-type explosive composition according to the invention preferably contains one or more combustible substances which have a negative oxygen balance, and are substantially stable and insoluble in water. In order to obtain the desired substantially homogeneous dispersion in the aqueous phase the particle size of any solid substance, i.e. combustible substances and solid oxygen carriers, present in the composition according to the invention should be below 500 microns and preferably below about 200 microns.

The term "combustible material" as used in the specification and the claims is intended to include any substance or composition which in a finely dispersed state is accessible to a relatively rapid combustion and which upon such combustion develops an appreciable heat of combustion, e.g. of from about 1000 to about 14,000 kilo-calories per kilogram of substance.

One preferred group of combustible materials includes conventional low velocity organic explosives having a velocity of detonation (standard value) of below 7500 meters per second, such as aromatic or aliphatic nitro compounds, e.g. trinitrotoluene, trinitronaphthalene, dinitronaphthalene, hexanitrodiphenylamine, tetranitromethylaniline, mononitrobenzene, mononitrotoluene, dinitrobenzene, dinitrotoluene, dinitronaphthalene, etc. It is to be noted that the lower nitro compounds mentioned above, i.e., those having one or two nitro groups normally are not considered to be explosives and it is one of the advantages of the present invention that even such compounds may be used singly or in combination in the preparation of explosive compositions according to the invention.

Another group of combustible materials includes metals, such as aluminium, magnesium, silicon, boron and other metals having a heat of combustion in the range specified above. However, the use of metals which upon combustion develop toxic products or which easily corrode in the presence of water is not preferred according to the invention. Alloys or mixtures of suitable metals may, of course, be used as well.

A further group of combustible materials includes carbonaceous organic substances, such as mineral oils, e.g. xylene, toluene, decane, diesel oil, kerosene, paraffinic oils, and other petroleum fractions, vegetable oils, e.g. castor oil, olive oil, linseed oil, etc., wood flour, paraffin, wax, etc. Volatile combustible compounds, such as benzene, hexane, etc. should not be used since they tend to evaporate from the composition and to form explosive gaseous mixtures. Also, care should be employed in selecting substances from this group since, as is well known in the art, some members of this group, e.g. paraffin or paraffin oil, have a tendency to desensitize a given explosive. Accordingly, such combustible materials should generally not be used in excessive amounts, e.g. less than 10% and preferably less than 5% by weight of the composition, or not at all, if the resulting mixture is desensitized to the point where ignition becomes problematic.

As previously mentioned, combustible materials from the group including high velocity explosive organic compounds, with a detonating velocity (standard value) of above 7500 meters per second (with the exclusion of liquid organic esters of nitric acid and particularly nitroglycerin) may be used in the compositions of the invention in amounts ranging from 0 to about 15% by weight of the entire composition. Explosive substances of this type include normally solid esters of nitric acid such as PETN, mannitolhexanitrate, hexogene (trimethylene trinitramine) and substances such as tetryl (trinitrophenyl methylnitramine), etc.

It is to be noted that these high velocity explosives eventually to be used in the compositions of the invention lose their well known booster function if present in the composition in relatively small amounts and in admixture with the other components. In contrast hereto, a booster charge is a separate, i.e. external, charge generating a relatively concentrated shock of detonation and thereby initiating the main explosive charge. Accordingly, the effectiveness of the high velocity explosives used according to the invention, i.e. in small amounts of less than 15% by weight and in admixture with an aqueous phase, is quite surprising.

A preferred dispersion-type blasting explosive composition according to the invention contains, besides the combustible material mentioned above, a solid and preferably inorganic oxygen carrier dispersed in the aqueous phase. The term "oxygen carrier" as used herein is intended to include substances having a positive oxygen balance as previously explained.

Organic oxygen carriers are not preferred due to the hazards involved and the relatively high costs of such substances. Preferred oxygen carriers according to the invention are inorganic substances having a positive oxygen balance, e.g. nitrates, chlorates, and perchlorates of ammonium, the alkali metals, the earth alkali metals, lead, e.g. ammonium nitrate and perchlorate, sodium and potassium nitrate, calcium nitrate, lead nitrate, sodium perchlorate. Relatively unstable or highly corrosive inorganic substances of this type, e.g. the peroxides, nitric acid, nitrogen tetroxide, etc. are not preferred. Several different solid oxygen carriers may be used but care should be taken so as not to select an unstable mixture. Inorganic nitrates are particularly preferred and from these ammonium nitrate is even more preferred due to its low costs and positive heat of combustion (381K cal./kg.).

The aqueous phase of the dispersion-type explosive compositions according to the invention comprises water, a swelling agent and a sufficient amount of dissolved oxygen carrier to impart a positive oxygen balance of at least 10 (or 10%) to the aqueous phase.

The swelling agent is a high molecular organic or inorganic material, e.g. having a molecular weight of above about 500 and preferably in the range of from about 5000 to about 500,000 or more, and must be soluble or swellable in water.

The essential function of the swelling agent is to increase the viscosity of the aqueous phase sufficiently in order to ensure that the dispersion resulting from addition of the other components of the explosive composition to the aqueous phase is of the desired stability, i.e. does not show undue sedimentation. Substantial sedimentation or segregation of the explosive composition should be avoided and a substantially uniform state of dispersion is desirable to ensure a maximum explosive effect and homogeneous detonation characteristics.

Substances of this type are well known in the art and only a few specific substances are mentioned below by way of example.

Generally, a swelling agent is a macromolecular hydrophilic substance and may be a synthetic or natural product. Examples for natural products of this type include water soluble proteins such as collagen, re-

spectively glutin, e.g. the various gelatines and organic glues containing a substantial amount of collagen or related substances; water soluble carbohydrates of the polysaccharide type such as starch, dextrine, dextrane; water soluble vegetable gums and resins such as tragacanth gum, arabic gum; natural plant hydrocolloids such as the alginates; etc. Synthetic macromolecular hydrophylic substances may be used as well and include synthetic polymers such as polyvinylalcohol, polyvinylpyrrolidone, polyvinylmethylether, methylcellulose, etc. Inorganic hydrocolloid forming substances such as the alkali metal silicates may also be used as swelling agents and the above mentioned substances may be used in combination. It is to be noted that many other known swelling agents singly or in combination may be used for the aqueous phase and that the selection of an appropriate substance is not critical.

It is preferred, however, that the desired viscosity of the aqueous phase is achieved with a relatively minor portion of the swelling agent or agents, e.g. in the range of from about 0.1% to about 10% by weight of the aqueous phase, the range of from about 1 to about 5% being preferred.

The aqueous phase must contain a sufficient amount of dissolved oxygen carrier of the type referred to above and have a high excess of oxygen, i.e. a strongly positive oxygen balance. Generally, the oxygen balance is at least +10%, the range from about +15 to about +25 being preferred. The upper limit is not critical.

It has been found that a high positive oxygen balance of the aqueous phase can be achieved in a surprisingly simple way by using the above mentioned conventional inorganic water soluble oxygen carriers, such as nitrates of ammonium, alkali metals and earth alkali metals, without an addition of expensive oxygen-yielding ingredients which tend to reduce safety. This can be achieved by using the so-called salting effect which enables a very high positive oxygen balance to be provided. At the same time, the sensitivity of the aqueous phase to low temperatures (recrystallization) may be considerably reduced, if appropriate quantity proportions are observed for a given system. For instance, if in a concentrated aqueous calcium nitrate solution contained solid calcium nitrate as solid sediment there is dissolved a second oxygen-yielding salt, such as ammonium nitrate, then, under isothermal conditions, more calcium nitrate can be dissolved from the solid sediment. The magnitude of this effect will become apparent from the following experiment:

A maximum of 127 g. of calcium nitrate can be dissolved in 100 g. of water at 20° C. However, in the presence of 50 g. of ammonium nitrate dissolved in this quantity of water, a further 56 g. of calcium nitrate are dissolved, so that a total of 183 g. of calcium nitrate may thus be dissolved in 100 g. of water. Using this procedure, a salt solution which even remains unsaturated at lower temperatures and which has a much higher total salt concentration (223 g.) and correspondingly higher oxygen balance has been prepared from a salt solution saturated at 20° C. with 127 g. of calcium nitrate.

Manganese nitrate or magnesium nitrate or any other oxygen-yielding salt having appropriate solubility, a high excess of oxygen and a low heat of decomposition can be used instead of calcium nitrate or in addition thereto to provide the salting effect, and systems having more than two salts can be prepared. The advantage of using several salts for the plasticizing agent is that a given value of oxygen excess can be achieved at a higher salt concentration and therefore with less water.

Primarily, the advantage of preparing a dispersion-type blasting explosive composition with an aqueous phase having a high oxygen surplus consists in the fact that such an aqueous phase can be used to plasticise or liquefy an oxygen deficient mixture of particulate solids, the resulting plastic or liquid dispersion-type explosive composition

having a balanced oxygen content. If in a given oxygen deficient prior art explosive mixture which is a dispersion of an oxygen deficient explosive substance and an oxygen carrier in an aqueous phase the portion of the oxygen carrier is to be increased in order to obtain oxygen balance of the mixture, the portion of the explosive substance is reduced concurrently. Since the explosive characteristics of such a mixture will usually depend largely from the oxygen deficient explosive substance present, a reduction of the amount of the latter will cause an undesirable deterioration of the explosive characteristics of the mixture particularly with regard to detonability.

If, however, in an oxygen deficient dispersion-type explosive composition an aqueous phase is used which, according to the invention, has a high oxygen surplus, a balanced oxygen content of the composition may be obtained without reduction of the portion of the oxygen deficient explosive substance.

Furthermore, the presence of an aqueous phase with a high oxygen surplus seems to sensitize dispersion-type explosive compositions and it is possible to prepare dispersion-type cap sensitive blasting explosives according to the invention with mono or dinitro aromatic compounds, e.g. mononitrobenzene or dinitrobenzene, as the only oxygen deficient compound present in the composition, even though such compounds normally are not considered as explosives.

A preferred aqueous phase according to the invention contains, for example, on a weight basis, from about 20 to about 70% of water, from about 30 to about 80% of inorganic oxygen carriers dissolved in the water, and from about 1 to about 5% of swelling agent.

Preferred oxygen carriers for the aqueous phase include calcium nitrate, ammonium nitrate and sodium nitrate in portions of 20-45%, 10-30% and 1-5% respectively. A preferred swelling agent is gelatine, e.g. agar-agar.

According to a preferred embodiment of the invention the dispersion-type blasting explosive composition is substantially liquid and comprises from about 20 to about 40% of the above aqueous phase, from about 20 to about 35% of oxygen deficient explosive material, and from about 25 to about 60% of solid oxygen carrier, preferably ammonium nitrate.

In some cases the entire portion of oxygen carrier present in the composition may be dissolved in water, i.e. forms part of the aqueous phase.

According to another preferred embodiment of the invention the dispersion-type blasting explosive composition is plastic and comprises from about 20 to about 35% of oxygen deficient explosive (combustible) material, from about 40 to about 65% of solid inorganic oxygen carrier and preferably ammonium nitrate, and from about 15 to about 25% of an aqueous phase or plasticizing agent.

A preferred aqueous phase suitable as plasticizing agent contains 40-55% calcium nitrate, 10-30% ammonium nitrate, 0-5% sodium nitrate, 2-3% agar-agar, all dissolved in 20-35% water.

An aqueous phase suitable as a plasticizing agent preferably is prepared by adding the swelling agent or hydrophilic colloid to the salt solution. Conveniently, the swelling agent is introduced after the various salts have been dissolved, the swelling agent being introduced, for instance, in a quantity of 3% by weight or less relative to the quantity of plasticizing agent. If a colloid of appropriately high swelling ability or high viscosity in aqueous solution is used as the swelling agent, its portion may be reduced correspondingly.

In principle, the aqueous phase or the plasticizing agent may also be formed during the actual mixing of the explosive composition if, instead of a salt solution which contains a swelling agent, there is used merely an aqueous colloid or solution of a swelling agent which then

becomes saturated with salt during the mixing by dissolution of the solid water soluble constituent. However, this method has the disadvantage of requiring a longer mixing time and of yielding less satisfactory plasticity; also, there may be some hardening.

According to a preferred embodiment of the invention a dispersion-type plastic safety explosive composition may be prepared using ammonium nitrate and trinitrotoluene, possibly with an addition of small proportions (less than 15%) of high explosive ingredients such as nitropenta and/or finely divided metal. Preferably, the grain size of the solid ingredients present in the composition is 200 μ or less.

As mentioned before, the explosive composition may contain an oil, e.g. mineral or vegetable oils, or an oily substance, e.g. a liquid nitroaromatic or aliphatic component. In these and other instances it may be desirable to add a minor amount of a dispersing or emulsifying agent, such as a polyglycoether, a long chain aliphatic alcohol, e.g. lauryl alcohol, or any of the well known surface active substances contributing to the stability of aqueous emulsions or dispersions. Preferably, the portion of the dispersing agent or emulsifying agent does not exceed 1% by weight of the aqueous phase.

The following examples are intended to more specifically explain the novel dispersion-type explosive compositions according to the present invention. These examples are for the purpose of illustration only, and not to be construed as in limitation of the invention. Percentages and parts in the examples as well as in the entire specification are by weight unless otherwise noted.

Example 1

A cap sensitive plastic safety explosive composition is prepared as follows:

To an aqueous solution consisting of 42 parts calcium nitrate (anhydrous), 28 parts ammonium nitrate and 27.5 parts water there are added 2.5 parts of agar-agar.

19 parts of the resulting aqueous phase or plasticizing agent are mixed with 59.5 parts of solid ammonium nitrate having a particle size of below 200 microns, and 21.5 parts trinitrotoluene (grain size below 200 microns). Mixing is continued until a homogeneous dispersion results and a plastic mass is obtained. This product is an oxygen balanced (0.3% oxygen surplus) plastic explosive composition; it is cap sensitive, i.e., it can be detonated in enclosure by means of a standard blasting cap, e.g. cap No. 8, without a booster charge. Upon detonation the composition generates a heat of explosion of 980 kilocalories per kilogram of explosive (H_2O -steam), a gas volume of about 860 liters per kilogram of explosive.

The explosive composition is substantially insensitive to shock of impact. The aqueous phase has an oxygen balance of +24%. The plastic explosive composition obtained can be liquefied by addition of 5% of water without losing its essential detonation characteristics.

Example 2

2.5 parts agar-agar are dissolved in an aqueous solution of 41.5 parts calcium nitrate and 28.0 parts ammonium nitrate in 28.0 parts of water.

21 parts of the resulting viscous aqueous phase, which has an oxygen balance of +24%, are intimately mixed with 52.5 parts of ammonium nitrate (particle size below 200 microns), 19.5 parts of trinitrotoluene (particle size below 200 microns), and 7 parts of pentrit (particle size below 200 microns). A plastic material is obtained which is a uniform dispersion of the solid constituents in the aqueous phase. This product has a balanced oxygen content (+0.2%) and can be detonated in enclosure by means of a standard No. 8 cap, i.e. it is cap sensitive. Its heat of explosion is 1010 kilocalories per kilogram (H_2O -steam); the gas volume is 850 liters per

kilogram. The shock-of-impact height, measured according to the standard procedure with a 5 kg. hammer, is more than 150 cm.

This plastic explosive is, with regard to brisance and bulging of the standard lead block substantially equivalent to a prior art safety dynamite with a content of about 20% of nitroglycerin and a shock-of-impact height of 34-40 cm.

The plastic explosive according to this example may be liquefied by addition of 5 parts water per 100 parts of the plastic composition. The liquid explosive thus obtained is similar, with regard to its explosive characteristics, to the original plastic composition; the oxygen balance of the aqueous phase after dilution still is strongly positive, the oxygen balance of the composition remains unchanged.

Example 3

24.9 parts of the aqueous phase or plasticizing agent of Example 2 are intimately mixed with 47.8 parts of ammonium nitrate, 10.8 parts of trinitrotoluene, 10.0 parts pentrit and 6.5 parts aluminum flakes. All solid components of the composition have a particle size of below 200 microns. The explosion characteristics of this plastic dispersion-type explosive composition are as follows:

Heat of explosion	-----	1200K cal./kg. (H ₂ O-steam).
Gas volume	-----	765 liters/kg.
Oxygen balance	-----	+0.4%.
Shock of impact	-----	+150 cm.
Ignition	-----	No. 8 cap.

Example 4

A preferred aqueous phase according to the invention is prepared by dissolving 2.8 parts of agar-agar in an aqueous solution of 27.8 parts of ammonium nitrate and 41.6 parts of calcium nitrate (anhydrous) in 27.8 parts of water.

18 parts of the aqueous phase or plasticizing agent thus obtained are intimately mixed with 75 parts of ammonium nitrate (particle size about 100 μ) and 7 parts of mononitrobenzene. The plastic explosive thus obtained is detonable with cap No. 8 in enclosure; the compression value measured according to the Hess-test is 33%. The gross bulge-out in Trauzl's lead block is 390 cm.³. This explosive composition has a positive oxygen balance.

Example 5

This example describes a plastic explosive composition containing no organic substance apart from the swelling agent of the plasticizing agent. A thorough mixture is made of 61% of ammonium nitrate, 21.5% of the plasticizing agent as described in Example 4 and 17.5% aluminum. The solid ingredients have a grain size of 100 μ or less. This plastic mixture, which has a compensated oxygen balance, detonates with a No. 8 cap in the Hess closed compression test; the compression factor is 50%. The gross bulge-out in Trauzl's lead block is 590 cm.³.

Example 6

An intimate mixture is made of 19% of the plasticizing agent described in Example 4, 59.5% of ammonium nitrate and 21.5% of trinitrotoluene, a uniform dispersion-type composition of plastic consistency being thus provided. The grain size of the solids is less than 200 μ . This explosive has a compensated oxygen balance and can be detonated with conventional caps, that is without a booster charge.

Example 7

A mixture having a compensated oxygen balance is prepared from 19.0% of the plasticizing agent described in Example 4, 39.0% of ammonium nitrate, 20% of sodium nitrate and 22.0% of dinitrobenzene; the mixture can be detonated in enclosure with a No. 8 cap, i.e. without a booster charge. Hess closed compression value is 31%.

The gross bulge-out in Trauzl's lead block is 390 cm.³. This mixture is thoroughly plastic.

Example 8

A plastic explosive having a density of about 1.3 g./cm.³ is prepared from 77% of ammonium nitrate, 18% of the plasticizing agent described in Example 4 and 5% of diesel oil; the explosive can be detonated satisfactorily by means of a booster or a relay and a No. 8 cap in enclosure, even if the diameter of the charge is only about 35 mm. Hess closed compression value with relay ignition is 34%.

Example 9

An aqueous phase having a highly positive oxygen balance is prepared by dissolving 34.4 parts of calcium nitrate, 23.2 parts of ammonium nitrate in 40.4 parts of water and addition of 2.0 parts of agar-agar.

A particulate (particle size below 200 microns) mixture of 56.5 parts of ammonium nitrate and 20.5 parts of trinitrotoluene is liquefied by addition of 23.0 parts of the aqueous phase.

The dispersion-type liquid explosive thus obtained is detonable with a standard cap No. 8, has a balanced oxygen content, i.e. a compensated oxygen balance, is substantially insensitive to shock of impact and has the following characteristics:

Heat of explosion	-----	900-910K cal./kg.
Gas volume	-----	880 liters/kg.
Oxygen surplus	-----	0.3%.

Example 10

41 parts of calcium nitrate and 2 parts of potassium nitrate are dissolved in 55 parts of water and 2 parts of agar-agar are dissolved in the salt solution. 23 parts of the viscous solution are intimately mixed with 56.5 parts of ammonium nitrate (particle size below 200 microns) and 20.5 parts of trinitrotoluene (particle size below 200 microns).

The resulting liquid composition has a compensated (+0.3%) oxygen content and is a dispersion of solid ammonium nitrate and trinitrotoluene in an aqueous phase having an oxygen surplus of more than 18%. The heat of explosion corresponds to 902K cal./kg. (H₂O-steam), the gas volume is 880 liters/kg. Ignition in enclosure can be effected by a No. 8 cap.

Example 11

26.5 parts of ammonium nitrate, 45.0 parts of calcium nitrate, 4.5 parts of barium nitrate are dissolved in 20 parts of water. In the resulting salt solution, 3 parts of dextrine are dissolved and 0.5 part castor oil are emulgated in the viscous solution by addition of 0.5 part propylglycol.

19 parts of the aqueous phase or plasticizing agent thus obtained are mixed with 59.5 parts of ammonium nitrate and 21.5 parts of trinitrotoluene, both in particulate form and having a grain size of below 200 microns.

The plastic dispersion-type explosive thus obtained has the following characteristics:

Heat of explosion	----	980K cal./kg. (H ₂ O-stream).
Gas volume	-----	860 liters/kg.
Oxygen balance	-----	+0.3%.
Ignition	-----	No. 8 cap.

Example 12

9.0 parts of ammonium nitrate and 31.0 parts of calcium nitrate are dissolved in 58.1 parts of water. 1.5 parts of dextrine and 0.4 part of propylglycol are dissolved in the aqueous salt solution.

The aqueous phase thus obtained has a high oxygen surplus.

A liquid dispersion-type explosive composition is prepared from 34.0 parts of this aqueous phase, 42.1 parts

of ammonium nitrate, 9.4 parts of trinitrotoluene, 8.8 parts of pertrit and 5.7 parts of aluminum flakes. All solid components have a particle size of below 500 microns.

The components are thoroughly mixed. The resulting composition has the following explosive characteristics:

Heat of explosion ----- 963K cal./kg. (H₂O-steam).
 Gas volume ----- 820 liters/kg.
 Oxygen surplus ----- 0.4%.
 Ignition ----- Cap No. 8.

The test methods by Trauzl and Hess mentioned in Examples 4-8 are described on pages 111 and 113 of the book by Stettbacher cited above. The only change effected for testing of the present compositions concerned the container in the Hess-test. A 100 mm.-steel tube having an inner diameter of 35 mm. and an outer diameter of 40 mm. was employed to hold the test charge. A sufficient amount of the charge was used to completely fill the tube.

Since it is obvious that many changes and modifications can be made in the above described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

Having thus described the invention, what is desired to be secured by U.S. Letters Patent is:

1. In a dispersion-type blasting explosive composition, wherein the composition comprises a non-aqueous phase containing combustible material dispersed but not dissolved in a aqueous phase with the aqueous phase comprising water, a swelling agent and an oxygen carrier dissolved in the aqueous phase, the improvement which comprises that the amount of said oxygen carrier dissolved in the aqueous phase is sufficient to impart to such aqueous phase a positive oxygen balance of at least 10% by weight, said aqueous phase being present in the composition in an amount sufficient to at least compensate any oxygen deficiency of said composition upon detonation.

2. The improvement of claim 1, wherein said non-aqueous phase is a mixture of said combustible material and a particulate solid oxygen carrier.

3. The improvement of claim 1, wherein the composition has a balanced oxygen content and essentially consists of intimate mixture of 61 percent by weight of solid particulate ammonium nitrate and 17.5% by weight of particulate aluminum as the non-aqueous phase; and 21.5% by weight of a homogeneous plasticizing agent as the aqueous phase, said plasticizing agent essentially consisting of 27.8% by weight of water, 27.8% by weight of ammonium nitrate, 41.6% by weight of calcium nitrate and of 2.8% by weight of agar-agar.

4. The improvement of claim 1, wherein the composition has a balanced oxygen content and essentially consists of 77% by weight of solid particulate ammonium nitrate and 5% by weight of diesel oil as the non-aqueous phase, and of 18% by weight of a homogeneous plasticizing agent as the aqueous phase, said plasticizing agent essentially consisting of 27.8% by weight of water, 27.8% by weight of ammonium nitrate, 41.6% by weight of calcium nitrate, and 2.8% by weight of agar-agar.

5. The improvement of claim 1, wherein said aqueous phase consists essentially of water, a swelling agent and at least two inorganic oxygen carriers having a different oxygen content and being dissolved in said water, the dissolved quantity of the oxygen carrier having the higher

oxygen content being greater than corresponds to the solubility of said oxygen carrier in pure water, said aqueous phase having a positive oxygen balance of from 15 to 30% by weight.

6. A dispersion-type blasting explosive as claimed in claim 5, wherein said combustible material is selected from the group consisting of mono- and di-nitro derivatives of benzene, toluene and naphthalene.

7. The improvement of claim 1, wherein said composition is cap-sensitive, said non-aqueous phase being an oxygen deficient mixture of said combustible material and a solid oxygen carrier, said combustible material being an organic nitro-compound.

8. The improvement of claim 7, wherein said oxygen deficient mixture contains from 0 to 15% by weight of a high velocity explosive selected from the group consisting of normally solid esters of nitric acid, and nitramines.

9. The improvement of claim 7, wherein said oxygen deficient mixture contains a particulate metal selected from the group consisting of aluminum, magnesium, silicon, boron, and combinations thereof.

10. The improvement of claim 7, wherein said organic nitro compound is trinitrotoluene, and said solid oxygen carrier is ammonium nitrate.

11. The improvement of claim 7, wherein said aqueous phase essentially consists of from 40 to 55% by weight of calcium nitrate, from 10 to 30% by weight of ammonium nitrate, from 0 to 5% by weight of an alkali metal nitrate selected from the group consisting of sodium and potassium nitrate, from 2 to 3% by weight of agar-agar and from 20 to 35% by weight of water.

12. A cap sensitive dispersion-type blasting explosive composition as claimed in claim 7, wherein said composition contains from 0 to 15% by weight of a high velocity explosive selected from the group consisting of normally solid esters of nitric acid and nitramines.

13. In a process for the production of a dispersion-type explosive, wherein combustible material and solid oxygen carrier salt are mixed with an aqueous phase, the step of preparing said aqueous phase by admixing first and second oxygen carrier salts with water, at least one of said first and second oxygen carrier salts being present in an amount exceeding its solubility in pure water, the other one of said first and second oxygen carrier salts being capable of increasing the water solubility of said one oxygen carrier salt, whereby an aqueous solution of said first and second oxygen carrier salts is obtained which contains an amount of said one oxygen carrier salt in excess of the amount normally soluble in water.

14. In a process as in claim 13, wherein said one oxygen carrier salt is selected from the group consisting of calcium nitrate, magnesium nitrate, manganese nitrate and mixtures thereof, and the other of said first and second oxygen carrier salts being selected from the group consisting of ammonium nitrate, potassium nitrate, sodium nitrate and mixtures thereof.

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CARL D. QUARFORTH, *Primary Examiner*.