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GAS-PRODUCING NONDETONATING COMPOSITION

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The present invention relates to gas pressure operated devices, for example to mechanical devices such as piston-actuated mechanism or to blasting cartridges of the kind comprising a pressure-resistant vessel and a pressure-responsive venting device, and in particular to new and improved charges for such devices. The invention relates in particular to such charges comprising compositions in which ammonium nitrate is the principal or sole gas producing agent.

When ammonium nitrate is heated to a temperature between 150°C and 360°C, unconfined and under ordinary pressure, a decomposition into nitrous oxide and water takes place which, although exothermic, requires a continuous supply of heat for its maintenance. This reaction is a well-known laboratory method for preparing nitrous oxide, and experience has shown that in carrying out the preparation an excessive supply of heat should be avoided, since the ammonium nitrate may otherwise itself detonate. If to ammonium nitrate there is added a combustible material, e.g., a carbonaceous material or a finely divided metal, capable of undergoing rapid oxidation by the available oxygen of the ammonium nitrate, the decomposition of the resultant mixture is more highly exothermic than that of the ammonium nitrate alone. Like ammonium nitrate itself, such mixtures are often too insensitive to be ignited or to be capable of self-sustained decomposition merely on local heating when unconfined, and, on the other hand, some of them are still more liable to detonate on heating in a confined space. The sensitivity to ignition and to self-sustained decomposition on local heating when unconfined depends on the nature of the combustible material and on the proportion thereof relative to the proportion of ammonium nitrate. When using carbonaceous ingredients as combustible material the tendency is for the sensitivity to increase with an increase in the proportion of the said carbonaceous material from that resulting in the formation of carbon dioxide to that resulting in the formation of carbon monoxide. As would be expected, other factors come into question such as the state of aggregation and consolidation of the mixture.

As an example of the influence of the proportion of ammonium nitrate on the ease of ignition, it may be stated that a solid mixture of 80 parts by weight of ammonium nitrate and 5 parts by weight of charcoal, although theoretically a balanced combustible composition in which there is sufficient ammonium nitrate to oxidise the carbon completely to carbon dioxide, is not capable of sustaining its decomposition at ordinary pressure when heated locally, for example by means of a fusee. On the other hand, a mixture in the same form of 80 parts by weight of ammonium nitrate and 12 parts by weight of charcoal burns quite easily at ordinary pressure when ignited by a fusee, the proportion of ammonium nitrate in this case being only sufficient to oxidise the carbon to carbon monoxide. The former composition under pressure shows a greater liability to detonation than the latter.

According to the present invention a charge for gas-pressure operated devices of the kind described comprises a gas-evolving component and a non-detonating igniting element insufficient of itself to effect any substantial general rise in the temperature of the charge, the said gas-evolving composition consisting essentially or largely of ammonium nitrate and containing as sensitiser chromic oxide or a chromium compound adapted to generate the same on heating in the presence of the ammonium nitrate, so that the said gas-evolving composition is capable of undergoing a self-sustained decomposition without detonation when ignited locally and at ordinary pressure by the said heating element.

The preferred sensitising materials for use in the charges of the present invention are ammonium or potassium dichromates or chromates, but the chromates or polychromates of other alkali metals, e.g., sodium, may also be used, while lead chromate and chromic chloride have also a slight sensitising effect and are included without the scope of the invention. It is considered that the active sensitising agent is probably freshly prepared chromic oxide since it has been found that the sensitising effect of the freshly prepared ash obtained by heating ammonium dichromate diminishes after a time. It will be understood that the charge may include ingredients other than ammonium nitrate which are capable of reacting with suitable chromium compounds to generate chromic oxide on heating. Such ingredients together with said chrom-
tum compounds will be understood to be equivalent to the chromates or polychromates referred to above.

The proportion of the chromate or polychromate required will not usually exceed 20% of the weight of the ammonium nitrate, but in most cases very considerably smaller proportions will be quite sufficient. It will usually be sufficient to employ about 1% to 10% of the weight of the ammonium nitrate. The charges of the invention are therefore characterised by their low ash content.

The gas-evolving compositions used in the present invention are preferably such that, in the absence of the chronic oxide sensitisers, they are capable of undergoing a self-sustained gas-producing decomposition without detonation either when confined under pressure and ignited with the aid of a local and limited heating element, or when heated at ordinary pressure sufficiently to cause a substantial and general rise in temperature. Such compositions may contain, in addition to the ammonium nitrate, a proportion of an oxidisable material, for example combustible gas, a combustible material. Suitable oxidisable materials are starch, charcoal, peat, woodmeal, plant fibre, natural and artificial resins, waxes, bitumens, hydrocarbons, soaps, fats, oils, and many other organic materials, less combustible or incombusible materials such as formaldehyde polymers, ammonium carbonate and bicarbonate, ammonium oxalate, urea, guanidine and other nitrogenous organic substances, or even certain inorganic nitrogenous materials such as hydrate hydrate. Small proportions of inorganic materials such as silica, china clay, magnesium carbonate, chalk, or the like which are said to influence the decomposition of ammonium nitrate may also be included if desired.

The sensitising chromium compound is preferably distributed uniformly throughout the gas-evolving composition, and the sensitised material may be manufactured by admixing the chromium compound with the ammonium nitrate either before or after the addition to the latter of any other ingredients that may be desired. The admixture is conveniently effected by a milling operation.

In the charges of the present invention the sensitised composition is ignited with the aid of a local and limited igniting element, i.e., one which is insufficient of itself to effect any substantial general rise in the temperature of the charge. The igniting element employed should be non-detonating in character and must be capable of generating a flame, flash, spark or the like in contact with the gas-evolving composition. As examples of such igniting element there may be mentioned an electric powder fuse, a safety electric igniter or a small smokeless powder or cordite charge ignited in turn by a fusehead or percussion cap. It will be understood that the use of a percussion cap in this manner for accelerating the flame producing igniter is not equivalent to the use of a detonator and does not involve any risk of detonation of the gas-evolving composition.

It will be understood that in using the charges of the present invention, the pressure under which the gas is generated will rise very considerably as the decomposition proceeds, but it is a characteristic feature of the invention that the presence of the sensitising agent does not appreciably affect the liability of the composition to detonate under ordinary conditions. The decomposition of a considerable portion of the charge takes place at a temperature below that at which the unsensitised composition would have required to be heated before it commenced to decompose. The production of the pressure is thus achieved in a gradual fashion.

According to a particular form of the invention, a blasting device comprises a pressure-resistant metal vessel fitted with a pressure-responsive venting device and charged in the manner hereinbefore described with a sensitised ammonium nitrate composition and with a non-detonating igniter. The igniter may be a cartridge consisting of an electric powder fuse, but igniters of the kind described in British Specification No. 431,956 may also be employed. In blasting devices of this kind, the proportion of oxidisable material in the ammonium nitrate composition should preferably be sufficiently high to ensure that no appreciable proportion of free oxides of nitrogen is formed by the combustion.

In such blasting devices it is preferred, in general, that the proportions of ammonium nitrate and of oxidisable material should be such as to ensure that the main portion of the charge is burned practically completely to carbon dioxide and water. Ammonium nitrate mixtures of this kind are not usually themselves sufficiently sensitive to support their combustion at ordinary pressures when ignited with the aid of a local and limited igniting element, and consequently the present invention is of particular value in providing suitable charges for blasting devices of the kind described.

In preparing compositions for blasting in this manner and especially for use in fiery or dusty mines, incombusible materials, for example ammonium carbonate or bicarbonate or other incombusible materials yielding a high gas volume on oxidation, are particularly useful as materials for reacting with the excess oxygen of the ammonium nitrate composition. Such materials as ammonium carbonate or bicarbonate, which are themselves decomposable by heat with the production of gases, may themselves be introduced in greater quantities than required for the oxygen balance, and then serve a useful purpose in contributing to the pressure developed and in moderating the temperature attained. Moderate quantities may usually be introduced by simple admixture, but when it is desired to introduce considerable proportions of such materials, it is often convenient to employ a portion at least of the ammonium carbonate or the like in granular form well distributed throughout the remainder of the composition which may itself be in powder or in granular form and which contains the ammonium nitrate and sensitiser and advantageously also enough combustion material to balance the mixture.

In the blasting devices of the present invention the ammonium nitrate composition used may consist of any of the exothermic gas-evolving compositions set forth in British Specification No. 430,288, corresponding to U. S. Application Serial No. 712,035, filed February 16, 1934, such as 10% ammonium nitrate, guanidine nitrate, urea nitrate, and dicyandiamide nitrate, either alone or in mixtures. According to the said specification these gas-evolving compositions are employed in conjunction with a non-detonating
heating composition in substantial amount. According to the present invention, however, the gas-evolving compositions are employed in the presence of a chromium compound as sensitizer so that the compositions are rendered capable of supporting their own decomposition when ignited with the aid of a local and limited heating element, e.g., a 30 to 100 grain powder fuse.

When the blasting devices as above described are to be used in fiery or dusty mines it is desirable that any combustible organic ingredients present should be rendered incapable of being projected in flaming particles capable of igniting inflammable atmospheres, in order to minimise the risk of any such ingredients being vented while unconsumed or only partly consumed and still burning or taking fire. Such fireproofing may be effected by impregnation with fireproofing salts, for example ammonium phosphate or sulphate, sodium tungstate, alum or borax.

According to a further form of the present invention a gas-pressure operated mechanical device for example piston actuated mechanism or the like, includes a suitable gas-generating vessel or container and a charge of a sensitized ammonium nitrate composition and a non-detonating igniting element as hereinbefore described. In this form of the invention it is usually desirable that the proportion of oxidizable material should not only be sufficient to prevent the formation of free oxides of nitrogen or other corrosive gases, but also to yield a relatively high proportion of permanent gas. In the oxidation of a material composed of carbon and hydrogen and whether or not containing a proportion of oxygen in its composition; complete oxidation to carbon dioxide yields a smaller volume of permanent gas than oxidation to carbon monoxide and hydrogen, since in the latter case no diminution in the volume of the products due to the condensation of water vapour would be experienced.

In the operation of a mechanical device this may be of some importance, and accordingly it will not usually be desirable to minimise the formation of carbon monoxide as in the case of blasting.

The invention is further illustrated by the following examples in which the parts are by weight.

**Example 1**

100 parts of ammonium nitrate were milled with 6 parts of ammonium dichromate and 6 parts of charcoal in an edge runner mill until the ingredients were well distributed, the charcoal being added after the ammonium nitrate and ammonium dichromate had been lightly mixed. The loose powder when made into a loose train 1/4" deep was found to be capable of supporting its own combustion when ignited at one end by means of a fuse, whereas a composition made in similar fashion containing only the ammonium nitrate and water charcoal failed to support its combustion when similarly ignited. In order to take up the excess oxygen of the mixture and provide a further source of gas pressure and reduce the temperature of combustion somewhat there was further incorporated into the composition containing the three ingredients 20 parts of ammonium bicarbonate. The powder so obtained was still capable of supporting its combustion when locally ignited. A quantity of the powder was enclosed, together with an igniter consisting of a 100 grain powder fuse, in a pressure resisting vessel having a pressure responsive venting device. The so charged device was suitable for non-safety blasting purposes.

**Example 2**

A mixture of 80 parts ammonium nitrate powder, 8 parts powdered potassium chromate, 2 parts starch and 1 part china clay were milled together until the ingredients were thoroughly mixed. In the resulting powder there was stirred one third of its weight of ammonium bicarbonate granules. The composition was used in a blasting device in the manner described in Example 1 and the so charged device was suitable for use in a fiery or dusty mine.

**Example 3**

A mixture of ammonium nitrate, starch; ammonium dichromate and china clay in the proportions 80:2:5:1 was milled with a sufficient quantity of water to make a stiff paste for half an hour and then spread out in layers about 3/4" thick and dried. The dried cake was broken down and sieved, the granules retained on a sieve having 20 meshes to the inch but passing a sieve of 6 meshes to the inch being taken. The granulated material was mixed with one third of its weight of ammonium bicarbonate granules to about the same size. A charge of 215 gms. of the composite mixture were loaded into a pressure resistant steel tube blasting device having a capacity of 600 cc's and venting at a pressure of 12 tons/sq. in., there being also included an electric powder fuse containing 100 grains of black powder as igniting agent. The charged device when tested by firing in a gallery containing 9% methane air mixture or containing coal dust gave no ignition.

**Example 4**

This example illustrates the use of fireproofed woodmeal. 10 parts of woodmeal were soaked in a solution containing 2 parts by weight of ammonium sulphate and 2 parts by weight of di-ammonium hydrogen phosphate dissolved in as little water as possible, mixing up the woodmeal with the solution for some hours. The fireproofed woodmeal was then dried, and mixed into a mixture of ammonium nitrate, basic magnesium carbonate and ammonium dichromate in the proportion of 5 parts woodmeal to 7 parts ammonium nitrate and ½ part each ammonium dichromate and basic magnesium carbonate. The mixture was used in a blasting device in the manner described in Example 1, the igniter consisting however of a 60 grain powder fuse. The charged device was suitable for use in fiery or dusty mines.

**Example 5**

7 parts of mineral jelly were mixed into a previously prepared mixture of 80 parts ammonium nitrate and 8 parts of ammonium dichromate, and the mixture was pressed into the form of a pellet. This composition is capable of supporting its own combustion with the evolution of carbon dioxide and water vapour and was associated with an igniter consisting of a small silicon saltpetre charge itself ignited by a percussion cap. The resulting charge was suitable for use in gas pressure operated mechanical devices.

**Example 6**

A charge as in Example 5 included a composition prepared by pressing into the form of a cartridge a mixture containing 80 parts ammonium nitrate; 10 parts bitumen and 5 parts ammonium dichromate. Somewhat slower burning compositions were obtained by using the ingredients in the proportions 80:5:5 and 80:2:3 instead of 80:10:5.
Example 7

A charge as in Example 5 included a composition made by pressing into the form of a rod a mixture of 80 parts ammonium nitrate, 5 parts paraformaldehyde, and 5 parts ammonium dichromate.

In order to disclose this application of my invention, reference is made to the appended drawing which illustrates a preferred embodiment thereof. It is to be understood, however, that this is done by way of illustration and is not to be regarded as a limitation upon the scope of my invention.

Referring to the drawing, the blasting device illustrated comprises a strong steel container 1, provided at one end with a firing head 2 separated from the container 1 by a sealing washer 9 of fiber or other suitable material such that a seal which is gas-tight at very high pressures is assured. The firing head 2 is provided with electrodes 7 and 8, one of which (8) is in metallic connection with the firing head 2, while the other electrode (7) is insulated therefrom. The mounting of the insulated electrode is such as to allow no leakage at pressures up to about 25 tons per square inch. Terminals 10 and 11 are provided for the electrodes which are used in initiating the cartridge electrically. A protective steel cap 3 having an aperture 14 for the leads of the terminals from the blasting machine or other suitable source of electric energy, is screwed on the firing head 2.

The blasting charge 13 comprising any of the gas-generating compositions in accordance with my invention, for example the composition of Example 1, is introduced loosely into the tube in the required amount. On the shoulder of the container remote from the firing head 2 is placed a fiber or light sealing washer 6 and a steel bursting disc 5 adapted to be ruptured at a predetermined and considerable pressure, both of these devices being held in position by the hollow screw in cap 4, which is placed with suitable channels for venting the gases and directing and distributing the blast. An electric power fuse or safety igniter 12 containing, for example, 30 grams of block powder, is used for ignition and provided with long leads from the electrodes 6 and 7 and no connection as shown in the drawing so that the flash is directed toward the firing head. By so positioning the cap, the tendency of the adjacent charge to be forced into the plug at the end nearest the cap 4 is overcome.

For convenience, the device has been shown in the upright position, but it will be understood that the charge 13 would only assume this position if the device were horizontal. In practice, the device may be used in any position so long as there is effective contact between the fuse 12 and the charge 13.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:

1. In a pressure-operated device, in combination a pressure-resistant, pressure-responsive container, deflagrating ignition means and a deflagrating gas-generating composition capable of undergoing self-sustaining decomposition without detonation, said composition comprising ammonium nitrate, a carbonaceous substance which combines exothermically with oxygen and at least 1% of a substance comprising at least one member of the group consisting of chronic oxide, alkali metal chromates, ammonium nitrate, ammonium dichromate, and alkali metal polychromates, and a deflagrating gas-generating composition capable of undergoing self-sustaining decomposition without detonation, said composition comprising at least one substance selected from the group consisting of ammonium nitrate, guanidine nitrate, urea nitrate and dicyandiamide nitrate; a carbonaceous substance which combines exothermically with oxygen and at least approximately 1% of a sensitizing agent comprising at least one member of the group consisting of chronic oxide, alkali metal chromates, ammonium nitrate, ammonium dichromate, and alkali metal polychromates.

2. In a pressure-operated device, in combination a pressure-resistant, pressure-responsive container, deflagrating ignition means and a deflagrating gas-generating composition capable of undergoing self-sustaining decomposition without detonation, said composition comprising at least one substance selected from the group consisting of ammonium nitrate, guanidine nitrate, urea nitrate and dicyandiamide nitrate; a carbonaceous substance which combines exothermically with oxygen and at least approximately 1% of a sensitizing agent comprising at least one member of the group consisting of chronic oxide, alkali metal chromates, ammonium nitrate, ammonium dichromate, and alkali metal polychromates.

3. In a pressure-operated device, in combination a pressure-resistant, pressure-responsive container, deflagrating ignition means and a deflagrating gas-generating composition capable of undergoing self-sustaining decomposition without detonation, said composition comprising at least one substance selected from the group consisting of ammonium nitrate, guanidine nitrate, urea nitrate and dicyandiamide nitrate; a carbonaceous substance which combines exothermically with oxygen and at least approximately 1% of a sensitizing agent comprising at least one member of the group consisting of chronic oxide, alkali metal chromates, ammonium nitrate, ammonium dichromate, and alkali metal polychromates.

4. In a pressure-operated device, in combination a pressure-resistant, pressure-responsive container, deflagrating ignition means and a deflagrating gas-generating composition capable of undergoing self-sustaining decomposition without detonation, said composition comprising at least one substance selected from the group consisting of ammonium nitrate, guanidine nitrate, urea nitrate and dicyandiamide nitrate; a carbonaceous substance which combines exothermically with oxygen and at least approximately 1% of a sensitizing agent comprising at least one member of the group consisting of chronic oxide, alkali metal chromates, ammonium nitrate, ammonium dichromate, and alkali metal polychromates.

5. In a pressure-operated device, in combination a pressure-resistant, pressure-responsive container, deflagrating ignition means and a deflagrating gas-generating composition capable of undergoing self-sustaining decomposition without detonation, said composition comprising at least one substance selected from the group consisting of ammonium nitrate, guanidine nitrate, urea nitrate and dicyandiamide nitrate; a carbonaceous substance which combines exothermically with oxygen and at least approximately 1% of a sensitizing agent comprising at least one member of the group consisting of chronic oxide, alkali metal chromates, ammonium nitrate, ammonium dichromate, and alkali metal polychromates.

6. In a pressure-operated device, in combination a pressure-resistant, pressure-responsive container, deflagrating ignition means and a deflagrating gas-generating composition capable of undergoing self-sustaining decomposition without detonation, said composition comprising at least one substance selected from the group consisting of ammonium nitrate, guanidine nitrate, urea nitrate and dicyandiamide nitrate; a carbonaceous material and at least 1% of ammonium dichromate.

7. In a pressure-operated device, in combination a pressure-resistant, pressure-responsive container, deflagrating ignition means and a deflagrating gas-generating composition capable of undergoing self-sustaining decomposition without detonation, said composition comprising
at least one substance selected from the group consisting of ammonium nitrate, guanidine nitrate, urea nitrate and dicyandiamide nitrate; a carbonaceous material, a cooling salt, and from 1 to 20% of a sensitizing agent comprising at least one member of the group consisting of chromic oxide, alkali metal chromates, ammonium chromate, ammonium dichromate, and alkali metal polychromates.

8. The combination of claim 7, in which said cooling salt comprises ammonium bicarbonate.

9. A non-detonating gas generating composition capable of undergoing a self-sustaining decomposition without detonation, said composition comprising at least one substance selected from the group consisting of ammonium nitrate, guanidine nitrate, urea nitrate, dicyandiamide nitrate; a carbonaceous material, and from 1 to 20% of a sensitizing agent comprising at least one member of the group consisting of chromic oxide, alkali metal chromates, ammonium chromate, ammonium dichromate and alkali metal polychromates.

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CERTIFICATE OF CORRECTION.


JAMES TAYLOR.

May 23, 1939.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 45, for the word "without" read within; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 11th day of July, A. D. 1939.

Henry Van Arsdale

Acting Commissioner of Patents.