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EXPLOSIVE COMPOSITION

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14 Claims. (Cl. 52-6)

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This invention relates to a new and improved granular detonating explosive composition of a free flowing type suitable for use in quarrying, open cut and stripping operations.

An explosive of this type is characterized as a 5 detonating or high explosive in distinction from a deflagrating or low explosive such as black powder.

Important factors involved in a suitable explosive for quarrying operations include free 10 flowing characteristics, rate of detonation, sensitivity and safety.

In modern quarry operations a free flowing explosive is poured from bags into either large diameter drill holes of considerable depth or into 15 a chamber produced by springing a cavity in a small diameter drill hole by a previous charge of a high explosive. In order that the powder may be loaded uniformly without air gaps due to the explosive "bridging over" in the column, it is 20 necessary for the powder to have good free running characteristics and be non-cohesive and granular in character.

The rate of detonation refers to the velocity of propagation of the explosive wave in a column of 25explosive. It is measured in cartridges of  $1\frac{1}{4}$ inch diameter by the Dautriche method. In modern quarry practice detonating explosives of relatively low rates of detonation are preferred since it has been found that such explosives, by 30 their sustained heaving action, throw the burden from the face and thereby reduce the amount of secondary blasting.

The sensitivity of an explosive composition is a measure of its ability to be detonated. It is 35 important that an explosive of this type is able to be initiated by a commercial blasting cap or by detonating fuse.

An object of this invention is the production of a detonating explosive composition of good free  $_{40}$ flowing qualities having a low velocity of detonation and high sensitivity. A further object is the production of such an explosive which will not decrease in sensitivity or strength when stored for long periods of time. Another object is the 45 production of a detonating explosive which is economical to manufacture. An additional object is the production of an explosive composition characterized by great safety in use and in manufacture produced by combining ingredients which 50 a coating of a binder 7 thereon, and a pulverulent are in themselves substantially incapable of detonation.

Prior art explosives of the free flowing type having low velocities of detonation have suffered 2

fail to propagate in columns of small diameter. Further, some of these compositions are not capsensitive and must be initiated by a booster charge of a high explosive.

The compositions of the present invention have low rates of detonation of the order of 5000 ft./sec. yet are sensitive enough to be initiated by a commercial #6 blasting cap, or by detonating fuse, and propagate in column diameters as low as % inch. These compositions may be utilized in cartridges as well as in bags if desired.

These objects are attained in my invention by a novel type of granular explosive composition in which the core of the grain does not consist of an explosive element, but consists of a combustible element which is easily volatilized enveloped with an adherent layer of an explosive composition. The combustible element is sulfur which is used as the core of the grains and is the principal ingredient.

In order to make the explosive layer adhere to the sulfur granules, they are first wet with a binding agent which is liquid at moderate temperatures so as to form a film on the granules of sulfur.

Binding agents having suitable characteristics for this application are the aromatic nitro compounds which are liquefiable at moderate temperatures. Examples are the mononitro and dinitro derivatives of toluene, benzene or napthalene. The preferred component is dinitrotoluene.

For the explosive layer which forms the surface of the grains of these compositions, an intimate mixture of pulverized ammonium nitrate with a suitable sensitizer is preferred. However, other pulverulent explosives known in the art, such as nitrostarch, may be used to replace, in whole or part, the ammonium nitrate and sensitizer.

In the drawings, there is shown in Figure 1 an enlarged view, in cross-section, of sulfur granules suitable for use in the present invention.

In Figure 2, the sulfur granules are shown after they have been treated with a binder.

In Figure 3, the sulfur granules are shown after they have been treated with both a binder and a pulverulent explosive.

Referring to the drawings by reference characters, there are shown sulfur granules 5 having explosive 9 forming the surface layer of the finished explosive.

Many sensitizers for ammonium nitrate are known in the art, such as carbonaceous combusfrom such a low degree of sensitivity that they 55 tible materials, nitrostarch, or certain finely

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powdered easily oxidizable metals. Of the latter class either powdered magnesium or powdered aluminum may be employed. I prefer powdered aluminum by reason of its high heat of combustion and for economic and safety considerations. However, aluminum may be used in conjunction with other sensitizers such as nitrostarch and/or carbonaceous combustible materials.

The order of mixing the ingredients is critical, a layer of the explosive ingredient, held by the binding agent, the objects of my invention are Thus if the sulfur granules are not not attained. coated with the binding agent before the addition of the fine ingredients, that is, if the liquid binding agent is first added to the fine ingredients, the surface of the sulfur granules is not wet by the binding agent and as a result a layer of the explosive does not adhere to them. A com-20position mixed in this way, in which the granules of sulfur are not enveloped by a layer of the explosive component, held by the binding agent, results in a composition which, upon initiation, will not propagate even the length of a single 1<sup>1</sup>/<sub>4</sub>" x 8" cartridge, since the uncoated sulfur, which forms the major component in the mixture, blanks off the detonation wave. However, when the sulfur granules are first wet with the binding agent and then the explosive components are added so that a layer envelops the sulfur  $^{\rm 30}$ granules the resulting mixture will propagate continuously upon detonation in cartridge diameters as low as  $\frac{7}{8}$ ".

These facts prove the principle of my invention by means of which the continuous volatilization of the large sulfur component with the detonation wave has been achieved.

The finished composition is in the form of a loose aggregate of individual coated grains. In 40 certain of these compositions in which a high proportion of the fine ingredients is present some excess of the fine ingredients may not be held on the surface of the grains. However, if the sulfur granules are coated, the composition is still substantially granular in character, and the favorable free flowing characteristics and ballistic properties are unchanged. For this reason I do not wish to be limited to compositions in which all of the fine ingredients must be bound to the sulfur granules. Also in certain formulations where a high proportion of the fine ingredients are present two or more layers may be held on the surface of the grains by repeating the addition of binding agent and fine ingredients after the first layer is bound.

My preferred explosive composition consists of the following ingredients:

Percer	nt by	Ŵ	ight	
Sulfur granules	93.5	to	56.0	
Powdered aluminum	.5	to	8.0	
Nitroaromatic compound	1.0	to	8.0	
Ammonium nitrate	5.0	to	28.0	

The sulfur used in these compositions should have a minimum size which allows substantially 65 all of the particles to be retained on a 40 mesh standard testing screen. Below this size the free flowing characteristics of the compositions are affected. Above this size a wide range of particle sizes is possible so that, for example, run-of-mill roushed sulfur in the range of from minus 6 mesh to plus 40 mesh may be used. Sulfur that has been formed into pellets from the molten state, for example, by cooling drops of melted sulfur in air or in water may also be used. **75** 

The ammonium nitrate used in these compositions should be a fine powder, preferably below 100 mesh, intimately mixed with finely powdered aluminum. It is possible to replace up to five or ten percent of the ammonium nitrate with so-

dium nitrate, but no advantage is gained thereby. These compositions are manufactured in the following manner:

The order of mixing the ingredients is critical, since, if the sulfur granules are not coated with a layer of the explosive ingredient, held by the binding agent, the objects of my invention are not attained. Thus if the sulfur granules are not coated with the binding agent before the addi-

15 aluminum, preferably previously mixed, is added and the tumbling continued until the sulfur granules are coated with a layer of the mixture which is bound to the granules as the film of binding agent cools and hardens. It is preferable but not
20 necessary that the fine ingredients be pre-mixed before they are added.

I am aware of detonating explosive compositions of the granular type in which the grains consist of the oxidizing explosive elements am-

25 monium nitrate or sodium nitrate either alone or in intimate contact with sensitizers, fuel elements, or both. The grains of certain of these compositions are coated with sensitizers or a combination of explosive component and sensitizer.

30 Although sulfur has been often used as a fuel element in the prior art of detonating explosives in relatively small proportions and has been used in larger proportions in the prior art of deflagrating explosives, I am not aware of a detonating 35 explosive of this type in which the grains consist of a core of sulfur coated with explosive elements and in which sulfur forms the principal ingredient of the composition.

The explosive characteristics of these novel 40 compositions differ in marked degree from those known in the prior art. Whereas the rate of detonation of prior art granular detonating explosives varies markedly with the grain size, the smaller grain sizes giving the higher rates, the 45 low rates of detonation of my compositions vary in only a small range for any given percentage

composition as the size of the sulfur grains is varied over a wide range.

These compositions are characterized by high  $_{50}$  pressure development upon detonation.

Although I do not wish to be bound by any theory as to the mechanism of the explosive action of this new composition, certain postulates may be made, based on its ballistics and physical and chemical constitution. This novel explosive 55 composition is characterized chemically by a very high oxygen deficiency due to its high sulfur content. The oxygen available from the decomposition of the ammonium nitrate is only approximately sufficient to oxidize the sensitizer present. 60 Therefore the sulfur cannot be oxidized to gaseous sulfur oxides to any material extent. However, since these compositions are characterized ballistically by high pressures developed from the 65 gases formed, the major part of the gases developed must be sulfur vapor in the elemental form. Since the mixture of ammonium nitrate and aluminum forming a layer on the sulfur granules has a flame temperature on detonation of well over 2000° C. and sulfur vaporizes at the low tem-70 perature of 445° C. this is evidently the case. The volatility of sulfur at these temperatures explains the fact that the size of the grains affects the velocity of detonation only slightly.

The brisance of these compositions may be

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varied by varying the ammonium nitrate content and the ratio of ammonium nitrate to sensitizer so that various strength grades may be produced to meet a range of blasting conditions.

#### Example 1

Per c	ent	
Sulfur (minus 10 mesh plus 40 mesh)	79	
Ammonium nitrate	15	
Powdered aluminum	3	10
Dinitrotoluene	3	10

This composition was prepared by adding hot, liquid dinitrotoluene to the sulfur in a tumbling jar, tumbling the mixture until the sulfur was 15 coated with a film of the liquid, and then adding the previously mixed aluminum and ammonium nitrate and again tumbling.

The composition was detonated by a #6 blasting cap. It propagated continuously in a column diameter of  $\frac{7}{8}$ ". It had a rate of detonation of 5550 ft./sec. The brisance of the compositon 20 was 8 millimeters as measured by the U.S. Bureau of Mines small lead block method.

#### Example 2

Per	cent	
Sulfur (minus 6 mesh plus 14 mesh)	89.0	
Ammonium nitrate	6.5	
Powdered aluminum	2.0	
Dinitrotoluene	2.5	30

This composition was prepared in similar fashion to that of Example 1 except that the aluminum was added last, but before the binding agent had cooled and set. 35

This compositon was detonated by a #6 blasting cap, propagated continuously in a column diameter of %", and had a rate of detonation in 1<sup>1</sup>/<sub>4</sub>" x 8" cartridges of 5100 ft./sec. Its brisance was 3 millimeters as measured by the U. S.  $_{40}$ Bureau of Mines small lead block method.

These compositons have been tested and approved for chemical stability and for resistance to friction and impact.

It can be seen that my new compositions rep-45resent a notable advance in the explosive art. They combine the features of high sensitivity with low velocity of detonation in a free flowing explosive. They cause no headaches from handling since they contain no nitroglycerine, and 50do not deteriorate in storage. They are safe to use and handle. Furthermore, due to the exceptionally low cost of the raw materials used and the simplicity of the methods of manufacture it is possible to offer these compositions to 55industry at a price substantially lower than that of other types of detonating explosives of the prior art.

In summation, I have disclosed an explosive composition of improved characteristics and per-60 formance and which is distinguished from those known heretofore by having a granular form with the center or core of each granule being a particle of sulfur of such size that another compatible component useful in providing the final 65 explosive composition is secured thereto as a layer or coating. Sulfur will generally provide from 50% to as much as 80% to 90% by weight of the final granular composition. The other explosive components named herein, e. g. ammo-70 nium nitrate and nitro-starch and the sensitizers for such components, are well-known in the art and any of those compatible with sulfur can be utilized. Also, while I have mentioned the nitrocompounds of the aromatic series as the pre- 75 sulfur.

ferred binders, other compatible binders can be employed as desired. I claim:

1. An explosive composition consisting essentially of a loose mass of granules each having a center consisting of a coarse sulfur particle, said center being coated with an intermediate binding layer of di-nitrotoluene and an outer layer of an intimate mixture of ammonium nitrate and a sensitizer therefor selected from the group consisting of powdered magnesium and powdered aluminum the quantity of sulfur constituting at least one-half of the total composition.

2. An explosive composition consisting essentially of a loose mass of granules each having a center consisting of a coarse sulfur particle of a size such that the particle is retained on a 40 mesh screen, said center being coated with an intermediate binding layer of di-nitrotoluene and an outer layer of an intimate mixture of ammonium nitrate and powdered aluminum the quantity of sulfur constituting at least one-half of the total composition.

3. A composition as in claim 1 wherein the  $_{25}$  sulfur provides in excess of 30% of the weight of the composition.

4. An explosive composition consisting essentially of a loose mass of granules each having a center consisting of a coarse sulfur particle, said center being coated with an intermediate binding layer of a nitro-compound of the aromatic series and an outer layer of ammonium nitrate and a sensitizer therefor, the quantity of sulfur constituting at least one-half of the total composition.

5. An explosive composition consisting essentially of a loose mass of granules each having a center consisting of a coarse sulfur particle, said center being coated with an intermediate binding layer of a nitro-compound of the aromatic series and an outer layer consisting essentially of an intimate mixture of a sensitizer and a pulverulent explosive selected from the group consisting of ammonium nitrate and nitro-starch the quantity of sulfur constituting at least onehalf of the total composition.

6. An explosive composition consisting essentially of a loose mass of granules each having a center consisting of a coarse sulfur particle, said center being coated with an intermediate binding layer of a nitro-compound of the aromatic series, an outer layer of an intimate mixture of ammonium nitrate and powdered aluminum, the quantity of sulfur constituting at least one-half of the total composition.

7. An explosive composition consisting essentially of a loose mass of granules each having a center consisting of a coarse sulfur particle, said center being coated with an intermediate binding layer of di-nitrotoluene and an outer layer of an intimate mixture of ammonium nitrate and a sensitizer therefor the quantity of sulfur constituting at least one-half of the total composition.

8. The steps in preparation of an explosive consisting in coating coarse sulfur particles, each of a size such that the particle is retained upon a 40 mesh screen, with a layer of a binder comprising a nitro-compound of the aromatic series, and then applying to the so-coated sulfur granules an outer layer of a pulverulent explosive consisting essentially of an intimate mixture of ammonium nitrate and a sensitizer therefor consisting essentially of powdered aluminum, the quantity of pulverulent explosive not exceeding the quantity of

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9. The steps in preparation of an explosive consisting in coating coarse sulfur particles with a layer of a binder consisting of a nitro-compound of the aromatic series and then applying to the so-coated sulfur granules an outer layer consisting essentially of ammonium nitrate and aluminum, the quantity of sulfur constituting at least one-half of the mixture.

10. The steps in preparation of an explosive consisting in coating coarse sulfur particles, each 10 of a size such that the particle is retained upon a 40 mesh screen, with a layer of a binder consisting essentially of a nitro-compound of the aromatic series, and then applying to the so-coated sulfur granules an outer layer of a pulverulent explosive consisting essentially of an intimate mixture of ammonium nitrate and a sensitizer therefor the quantity of sulfur constituting at least a half of the total composition.

11. The steps in preparation of an explosive 20 consisting in coating coarse sulfur particles with a plurality of alternate layers of a binder consisting of a nitro-compound of the aromatic series and an intimate mixture of a pulverulent explosive consisting essentially of ammonium nitrate 25 and a sensitizer therefor.

12. The steps in preparation of an explosive consisting in coating coarse sulfur particles, each of a size such that the particle is retained upon a 40 mesh screen, with a layer of a binder consisting essentially of a nitro-compound of the aromatic series, and then applying to the so-coated sulfur granules an outer layer of a pulverulent explosive consisting essentially of nitro-starch

the quantity of sulfur constituting at least a half of the total composition.

13. An explosive composition consisting essentially of a loose mass of granules, each having a center consisting of a coarse sulfur particle, said center being directly coated with a layer of a binder consisting of a nitro-compound of the aromatic series, each granule having a plurality of alternate layers of binder and an intimate mixture of a pulverulent explosive selected from the group consisting of ammonium nitrate and nitrostarch and a sensitizer therefor.

14. A detonating explosive composition consisting essentially of a loose mass of granules each having a center consisting of a coarse sulfur particle, said center being coated with an intermediate binding layer of a nitro compound of the aromatic series and an outer layer of an intimate mixture of ammonium nitrate and a sensitizer therefor selected from the group consisting of powdered magnesium and powdered aluminum, the quantity of sulfur constituting at least a half of the total composition.

### WARREN B. RICHARDSON.

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