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THICKENED INORGANIC OXIDIZER SALT EX-PLOSIVE SLURRY SENSITIZED WITH A SOLU-BLE POLYFLAVONOID
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#### ABSTRACT OF THE DISCLOSURE

The sensitivity of slurry explosive compositions comprising inorganic oxygen-supplying salts, a fuel, a thickener and a liquid carrier is substantially improved by incorporating in the composition a soluble polyflavonoid

This invention relates to explosive compositions comprising essentialy an inorganic oxygen-supplying salt, a sensitizer, a fuel, a thickener and a mutual solvent for 25 the inorganic salt and the sensitizer. In particular, the invention relates to a means whereby the sensitivity of such explosive compositions may be substantially improved.

Explosive compositions comprising an oxygen-supply- 30 ing salt such as, for example, ammonium nitrate, and a sensitizer and/or fuel together with a fluid solvent, disperser or carrier such as water, are known. These compositions are commonly referred to as slurry explosive compositions or, more generally, as slurry explosives. 35 Such slurry explosives may range in degree of firmness or consistency from highly viscous, plastic-like extrudable compositions to less viscous pumpable or pourable fluid-

Slurry explosive compositions of the aforementioned 40 types normally contain as essential ingredients widely known sensitizing and power enhancing materials and fuels such as, for example, finely divided light metal, finely divided carbon and the like. In some cases, it is particulate TNT, PETN, or smokeless powder to further improve the sensitivity or strength or both of the slurry explosives and thereby insure detonation and propagation. A wide range of such compositions are now known to the art.

For optimum reliability the known sensitizers employed in slurry explosives are either self-explosives or relatively expensive materials such as very finely divided light metal powders. Without such sensitizers, these slurry explosive compositions tend to be detonable only in large diameter charges with large primers. It has thus been necessary for the manufacturer of explosives to employ relatively large quantities of sensitizing material and fuel in slurry explosives in order to insure detonation and propagation. Such compositions, as well as being relatively expensive, are hazardous to handle and require special and costly precautions in manufacture, transportation, storage and use. Slurry explosive compositions containing self-explosives are, in turn, in most jurisdictions subject to regulatory restrictions in transportation and storage. Those that  $^{65}$ contain reactive sensitizers such as, for example, paintfine aluminium powder, tend to deteriorate and lose sensitivity on storage.

It has now been found that the aforementioned disadvantages may be overcome by employing as a sensitizer in slurry explosive compositions a soluble polyflavonoid.

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It is, therefore, an object of the present invention to provide a means whereby the sensitivity of a slurry explosive composition may be increased.

Another object of the invention is to provide a slurry explosive composition which may be detonated in boreholes of small diameter.

Another object of the invention is to provide a sensitive slurry explosive composition which is devoid of any self-explosives or other hazardous material.

A further object of the invention is to replace the known reliable sensitizers in slurry explosive compositions with a sensitizer that is much less costly and easily availa-

These and other objects of the invention will become 15 apparent from a consideration of the following description and claims.

The improved explosive composition of this invention comprises essentially at least one inorganic oxygen-supand a common solvent for the polyflavonoid and the in20 thickener and a mutual solvent, usually water, for the inorganic salt and the polyflavonoid.

The addition of a soluble polyflavonoid to a slurry explosive composition has the surprising and desirable effect of substantially increasing the sensitivity of the composition.

It is thus now possible to prepare useful and powerful, slurry explosive compositions which, though devoid of any self-explosive ingredient, may be detonated with ease in boreholes of small diameters. It is similarly now possible to prepare such compositions even containing additional sensitizing material such as, for example, finely divided aluminium, aluminium, alloy, silicon, ferrosilicon or ferrophosphorus or self-explosives which are more reliable to detonation and propagation than heretofore and which may be detonated in smaller diameter and with the use of smaller priming charges that has heretofore been possible.

Preferred blasting slurry explosive compositions of this invention contain from 30 to 90% by weight of at least one inorganic oxygen-supplying salt, from 0.1 to 25% by weight of a soluble polyflavonoid, from 1 to 30% by weight of a mutual solvent for the inorganic salt and the polyflavonoid, from 0.1 to 10% by weight of thickener and from 0 to 40% by weight of fuel, the proportions of advantageous to add a self-explosive ingredient such as 45 the ingredients being such that the oxygen balance of the total composition is from +15 to -35 grams of oxygen per 100 grams of finished explosive.

> A preferred inorganic oxygen-supplying salt for inclusion in the explosive compositions of this invention is ammonium nitrate. It is in some cases advantageous to replace some, suitably up to 50% or even up to 90%, of the ammonium nitrate by other metal nitrates such as sodium, barium, potassium and calcium nitrates. The particle size of the inorganic oxygen-supplying salts is not critical and powdered, granulated, or prilled forms may be used and part of the salts may be predissolved in all or part of the solvent.

> A preferred mutual solvent for the oxidizing salt and the soluble polyflavonoid is water. However, quite large proportions of the water may be replaced by organic solvents such as formamide, dimethyl sulfoxide and the lower glycols and alcohols. These solvents are polar liquids, readily miscible with water in all proportions and are effective solvents for ammonium nitrate and other inorganic salts. The replacement of water is limited only by the lack of solubility of the polyflavonoid in solvent mixtures of low water content.

> Where employed, the aluminium or aluminium alloy or other energetic metal or metalloids suitable for use in the explosive composition of this invention must be in finely divided form and may most suitably range from a

fine dust to a form not coarser than that which will pass through a size 6 Tyler mesh screen. For example, relatively inexpensive air-atomized aluminium powder, shredded foil or granules made from reclaimed scrap are suitable types. The use of the expensive paint-fine aluminium is not required to achieve high sensitivity in the explosive composition of this invention.

Useful particulate self-explosives which may be used in the explosive composition include, for example, trinitrotoluene (TNT) pentaerythritol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), composition B (mixture of TNT and RDX), pentolite (mixture of PETN and TNT), smokeless powder, nitrocellulose, nitrostarch and mixtures of these.

The gel-forming or thickening polysaccharides employed in the aqueous slurry form of the explosive of the invention are preferably mannogalactans such as guar gum or carab seed. Guar gum of the self-cross-linking type recently made available on a commercial scale may be suitably employed. Where either dimethyl sulfoxide or formamide is employed alone as the mutual solvent in the slurry, hydroxyethyl cellulose may be used as a suitable thickener. Where dimethyl sulfoxide, formamide or ethylene glycol is used in combination with water, guar flour, tamarind flour or starch are suitable thickeners. A number of modified and synthetic materials useful as thickeners can be selected which are appropriate to the solvents employed and will be obvious to those skilled in the art.

Metallic chromates suitable for use as cross linking agents for the polysaccharides in aqueous slurries are the same as those disclosed in Canadian Patent No. 729,-555 issued on Mar. 8, 1966, that is, a metallic chromate selected from the group consisting of sodium and potassium dichromate and zinc and barium chromate.

The soluble polyflavonoid sensitizers are polyphenolic extracts from wood or bark and are commercially available as a sodium salt and sold as the trademarked product "Rayflo-C" by Rayonier Inc., New York. The polyflavonoid useful as sensitizers in the composition of the invention may be characterized by the resultant persistant head of foam which is formed when from 0.5% to 2.0% by weight of polyflavonoid is stirred into an aqueous solution saturated in nitrates of ammonia and sodium. The polyflavonoid may be employed either as a dry powder or alternatively as a solution. Where a polyflavonoid solution is employed, for example, an aqueous solution, the water of solution may be employed as all or part of the aqueous medium of the explosive composition.

The explosive composition may be prepared by processes well known in the art employing simple mixing 50 procedures, the soluble polyflavonoid sensitizer being added at any convenient stage in the manufacture. The polyflavonoid sensitizer may similarly be employed where a slurry explosive composition is prepared for use at the

The following examples and table illustrate the improved explosive composition of this invention but the latter is in no manner to be limited in scope to the embodiments described.

## EXAMPLE 1

A series of six viscous slurry compositions were prepared containing as essential ingredients, particulate oreners. To three of the compositions was also added a known sensitizer, sodium lignosulphonate. To one composition was additionally added powdered aluminium. Four of the compositions had added thereto a polyflavonoid sensitizer. The compositions were packaged in 70 11/2 inch and 21/2 inch diameter cartridges and exposed to initiation by various means. The compositions devoid of polyflavonoid failed to detonate. The results are summarized in the table below, the quantities shown being expressed as percent by weight of the total.

TABLE						
Mix No	1	2	3	4	5	6
PETN	5. 0	5. 0	5.0	5. 0		
TNT	20.0	20.0	20. 0	20. 0		20. 0
Ammonium Nitrate	33.5	33.5	28.1	27.9	52.3	50.3
Sodium Nitrate	35.0	35.0	39.0	39.0	18.0	18.0
Urea	1.5		1.5	1.5	1. 2	1. 2
Aluminium powder	<b></b> -				18.0	<del>.</del>
Zn Chromate (stabilizer)			0.2	0.2		<del>.</del>
Tamarind flour			0.3	0, 3	0.8	0.8
Guar flour	0.5	0.5	0.4	0.4		
Solium lignosulphonate	1.0		1.0	1.0		
Polyflavonoid (sod. salt)		1.0		0.5	0.5	0.5
2-ethyl hexanol 1	<b>. .</b>			. <b>.</b>	0.2	0.2
				4.2	9.2	9.2
Density (gm./cc.)	1.31	1.27	1.42	1.36	1.34	1.20
Cartridge diameter, in	$1\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$	$2\frac{1}{2}$	21/2
Primary charge	(2)	(3)	(4)	(5)	(6) ~	(6) Z
	Mix No  PETN	Mix No	Mix No.         1         2           PETN.         5.0         5.0           TNT         20.0         20.0           Ammonium Nitrate         33.5         33.5           Sodium Nitrate         35.0         35.0           Urea.         1.5         1.5           Aluminium powder         2         2           Zn Chromate (stabilizer)         2           Tamarind flour         0.5         0.5           Solium lignosulphonate         1.0           Polyflavonoid (sod. salt)         1.0           2-ethyl hexanol 1         1           Water         3.5         3.5           Density (gm./cc.)         1.31         1.27           Cartridge diameter, in         1½         1½	Mix No.         1         2         3           PETN         5.0         5.0         5.0           TNT         20.0         20.0         20.0         20.0           Ammonium Nitrate         33.5         33.5         38.1         38.0         38.0         38.0         39.0         30.0         20.0 </td <td>Mix No.         1         2         3         4           PETN.         5.0         5.0         5.0         5.0         5.0           TNT         20.0         &lt;</td> <td>Mix No         1         2         3         4         5           PETN         5.0         5.0         5.0         5.0         5.0         5.0         5.0         5.0         7.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.2         20.2         20.2         20.2         1.5         1.2         1.5</td>	Mix No.         1         2         3         4           PETN.         5.0         5.0         5.0         5.0         5.0           TNT         20.0         <	Mix No         1         2         3         4         5           PETN         5.0         5.0         5.0         5.0         5.0         5.0         5.0         5.0         7.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.0         20.2         20.2         20.2         20.2         1.5         1.2         1.5

- 1 Employed to eliminate any large unstable air bubbles in mix.
  2 No. 8 Cap failed.
  3 One No. 8 Cap fired.
  4 No. 12 Cap failed.
  5 One No. 12 Cap fired.
  6 160 gm. pentolite fired.

It can be noted from the results shown in the table that Mixes 1 and 3, devoid of polyflavonoid yet containing a known sensitizer sodium lignosulphonate, failed to detonate while mixes 2 and 4 of similar composition and containing the polyflavonoid sensitizer were detonated with ease. Mix 5, devoid of any self-explosive ingredient was made sensitive by the addition of a small quantity of polyflavonoid.

## EXAMPLE 2

A slurry explosive composition was prepared containing as essential ingredients 53.0% by weight of ammonium nitrate, 18% by weight of sodium nitrate, 1.2% by weight of urea, 0.8% by weight of tamarind flour, 18% by weight of particulate aluminium and 9.0% by weight of water. The composition was packaged in 21/2 inch diameter cartridges and exposed to detonation by means of a 160 gm. pentolite primer. The composition failed to detonate. A similar composition containing 1.5% by weight of a polyflavonoid as a replacement for a like quantity of ammonium nitrate was easily detonated with a similar primer at a detonation velocity of 3580 meters/

## EXAMPLE 3

A slurry explosive composition was prepared containing as essential ingredients 27.2% by weight of ammonium nitrate, 20.0% by weight of sodium nitrate, 3.0% by weight of urea, 35.0% by weight of powdered aluminium, 0.3% by weight of zinc chromate, 0.5% by weight of guar flour, 10.0% by weight of water and 4.0% by weight of a polyflavonoid. The composition had a prepared density of 1.35 gm./ml. and detonated in a 2½ inch diameter cartridge at a detonation velocity of 4900 meters/second.

#### EXAMPLE 4

A slurry explosive composition was prepared containblasting site by means of the now well known slurry mix 55 ing as essential ingredients 62.5% by weight of ammonium nitrate, 12.6% by weight of sodium nitrate, 7.5% by weight of sulphur, 0.8% by weight of guar flour, 12.6% weight of water and 4.0% by weight of a polyflavonoid. The composition had a prepared density of 60 1.21 gm./cc. and detonated in a 21/2 inch diameter cartridge using a primer of 110 gms. of pentolite.

#### **EXAMPLE 5**

A slurry explosive composition was prepared containganic explosives, oxygen-supplying salts, water and thick- 65 ing as essential ingredients 69.4% by weight of ammonium nitrate, 15.0% by weight of powdered aluminium, 0.6% by weight of hydroxyethyl cellulose (thickener), 12.0% by weight of dimethyl sulfoxide, 2.0% by weight of water and 1.0% by weight of a polyflavonoid. The composition had a prepared density of 1.40 gm./cc. and detonated in a 21/2 inch cartridge using a primer of 320 gms. of pentolite.

As may be seen from the results shown in the preceding examples and table, the addition of a soluble polyflavo-75 noid to a slurry explosive composition has the surprising 5

effect of substantially increasing the sensitivity of the compositions. Slurry explosives of this type having an oxygen balance outside the range of +15 to -35 grams of oxygen per 100 grams of finished explosive make very uneconomical use of the available energy. It is preferred, therefore, that quantities of polyflavonoid sensitizer and fuel used be such that the oxygen balance of the composition is within the range +15 to -35.

It will be appreciated by those skilled in the art that the principal advantage to be enjoyed through the use of the polyflavonoid sensitized slurry explosive compositions of the invention lies in the utilization of non-self-explosive slurry composition. That is, slurry compositions comprising oxygen-supplying salts, a solvent for the oxygen-supplying salts and a fuel may now, by the addition of a suit- 15 able quantity of a polyflavonoid, be employed as practical and reliable commercial explosives possessing the additional advantages of low cost and great handling safety. Where it is desired to include in such compositions additional strength ingredients such as powdered light metal 20 salt. fuels or self-explosives, the use of the polyflavonoid sensitizers provides compositions which may be detonated in smaller diameter charges or with lower strength primers than has heretofore been possible.

The polyflavonoid sensitizers provide an additional 25 function in controlling the density of the explosive compositions since they are effective agents in preventing or arresting the dissipation of minute bubbles of air which have been entrained or occluded in the slurry mixture. Such air bubbles are normally incorporated in slurry explosive compositions by the lifting and folding of the mixture which occurs during the mechanical mixing of the ingredients or, alternatively, air is entrapped into the mixture in the voids of the dry ingredients. Such control of density is useful in permitting different loading and cartridging densities.

What we claim is:

1. An explosive composition comprising essentially at least one inorganic oxygen-supplying salt, a soluble polyflavonoid, a mutual solvent for the inorganic oxygen-supplying salt and the soluble polyflavonoid, a thickener and a fuel, the proportions of the indgredients being such that the oxygen balance of the total composition is from about +15 to about -35 grams of oxygen per 100 grams of finished explosive.

2. An explosive composition as claimed in claim 1

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wherein the fuel is selected from the group consisting of carbonaceous material, particulate organic explosives, particulate light metal or metalloids, sulphur, carbon, urea and mixtures thereof.

- 3. An explosive composition as claimed in claim 1 wherein the mutual solvent is water.
- 4. An explosive composition as claimed in claim 1 wherein the mutual solvent comprises a mixture of water and a miscible organic solvent selected from the group consisting of formamide, dimethyl sulfoxide, lower glycols and alcohols, the proportions being such as to permit a solubility of not less than 5 parts of polyflavonoid per 100 parts of the solvent mixture.
- 5. An explosive composition as claimed in claim 1 wherein the oxygen supplying salt is selected from the group consisting of the nitrates of ammonia, sodium, potassium, barium, calcium and mixtures thereof.
- 6. An explosive composition as claimed in claim 1 wherein the soluble polyflavonoid is present as its sodium salt
- 7. An explosive composition as claimed in claim 2 wherein the particulate organic explosive is selected from the group consisting of trinitrotoluene, pentaerythritol tetranitrate, cyclotrimethylenetrinitramine, mixture of trinitrotoluene and cyclotrimethylenetrinitramine, mixture of pentaerythritol tetranitrate, smokeless powder, nitrocellulose, nitrostarch and mixtures thereof.
- 8. An explosive composition comprising essentially between about 30% and about 90% by weight of an inorganic oxygen-supplying salt, between about 0.1% and 25% by weight of a soluble polyflavonoid, from about 1% to about 30% by weight of a mutual solvent for the inorganic oxygen-supplying salt and the soluble polyflavonoid, from about 0.1% to about 10% by weight of a thickener and from 0 to 40% by weight of a fuel, the oxygen balance of the total composition being from about +15 to about -35 grams of oxygen per 100 grams of finished explosive.

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