An explosive composition of matter comprising a major proportion of at least one inorganic oxygen releasing salt characterized in that the said salt is coated with an essentially complete coating of material comprising a hydrocarbon substance having hydrophobic or water repellent characteristics.

This invention relates to new water-resistant explosive compositions and to processes for their manufacture. In particular this invention relates to new explosive compositions which are in particular form and comprise a major proportion of inorganic oxygen releasing salt material and a minor proportion of material capable of reducing the rate of aqueous solution and leaching of the said inorganic salt on contact with water.

Because of the considerably lower cost of explosive compositions free of explosive nitric esters and nitro-compounds and because of the decreased hazards connected with their handling and storage, explosive compositions consisting essentially of inorganic salts often in combination with non-explosive fuel sensitizers, have gained wide acceptance in blasting operations. Such a composition is typically ammonium nitrate admixed with fuel oil. Much of the economy of such compositions is lost, however, because of the high water solubility of the inorganic salts. Inasmuch as a proportion of boreholes used in blasting operations contain small amounts of water either from seepage in the terrain or from surface water from rain the successful use of inorganic salt explosive compositions has been restricted either to boresholes which are dry or have been emptied of water. Alternatively the compositions have had to be used in a modified or packaged form which reduces the effect of water on the compositions. So as to protect such compositions from the effects of water it has been proposed to package such compositions in metal watertight containers. Such containers represent a substantial proportion of the cost of the explosive charge and furthermore lead to a reduction in the amount of charge which can be loaded into a borehole. It has also been proposed to use polymeric materials in the form of flexible film such as polyethylene film as a packaging material for such compositions. However such packages are prone to tear and puncture during insertion into a borehole past the jaggard projections in the walls and if a sufficient thickness of film to ensure against such puncturing is used much of the flexibility is lost and again full utilization of the borehole volume cannot be achieved.

We have now found that explosive compositions comprising a major proportion of an oxygen releasing salt or a mixture of such salts may be rendered less prone to attack by aqueous media if the composition is treated with a material comprising a substance having hydrophobic or water-repellent characteristics so as to coat the individual particles, grains or granules of the said oxygen releasing salt with a thin but essentially complete coating of said material.

Accordingly we provide an explosive composition of matter comprising a major proportion of at least one oxygen releasing salt selected from the group consisting of inorganic nitrates, chlorates and perchlorates, characterized in that the said oxygen releasing salt is coated with an essentially complete coating of material comprising a hydrocarbon substance having hydrophobic or water repellent characteristics.

Preferred hydrocarbon substances are asphalts, which are defined in accordance with the practice of the American Society for Testing and Materials as dark brown to black cementitious materials solid or semisolid in consistency, in which the predominating constituents are bitumens which occur in nature as such or are obtained as residua in refining petroleum. Additionally it may be said that asphalts characteristically contain a bitumen fraction insoluble in paraffin naphtha, the "asphaltene." So as to avoid confusion in terminology it is pointed out that under Australian, British and European usage asphalt as defined above is often referred to as "bitumen" or "asphaltic bitumen." However in the above definition of asphalts we mean by the term "bitumen" mixtures of hydrocarbons of natural or pyrogenous origin; or combinations of both, frequently accompanied by their non-metallic derivatives, and which may be gaseous, liquid, semisolid or solid and which are completely soluble in carbon disulphide.

Accordingly in an embodiment of our invention we provide an explosive composition of matter comprising a major proportion of at least one oxygen releasing salt selected from the group consisting of inorganic nitrates, chlorates and perchlorates, characterized in that the said oxygen releasing salt is coated with an essentially complete coating of a material comprising an asphaltic substance as hereinabove defined.

It is desirable that the compositions according to our invention should be substantially free flowing to facilitate positioning of them at a blasting site, e.g. transferring them to a borehole. Accordingly we provide in a preferred embodiment of our invention explosive compositions of matter as hereinbefore described characterized in that the coating comprises in addition an amount of an anti-agglomeration agent. By "anti-agglomeration agent" we mean one or more materials which reduces, minimizes or prevents agglomeration of the salt material to the extent that the coated salt particles remain in a substantially free flowing condition during and after coating. Thus the tendency of the particles to agglomerate or to form a coalescent mass is reduced when such an agent is incorporated in the coating.

Materials suitable for use as anti-agglomeration agents include organic and inorganic materials. From amongst these there may be mentioned polymeric materials e.g. polyesters; surfactants such as the alkylamines e.g. octadecylamine, or sulphonates e.g. sodium methyl naphthalene sulphonate; long chain acids e.g. stearic acid; finely divided naturally occurring materials e.g. Bentonite, clays, kaolin, mica or talc; or finely divided or comminuted metals.

Suitable finely comminuted metals are preferably selected from the group consisting of finely divided magnesium, aluminium, silicon, ferrosilicon, ferrophosphorus, titanium and boron. A particularly preferred finely comminuted metal is finely divided titanium. The degree of comminution of the metals is conveniently such that the bulk of the metal passes a 100 mesh sieve. It will be appreciated however that such metals are the more effective as anti-agglomeration agents as their degree of comminution increases. Thus for example metals passing a 200 mesh sieve or even a 300 mesh sieve are eminently suitable for use in our invention. Particularly suitable products are the commercially available so-called paint-fine
aluminums. Some of these paint-fine aluminums are comminuted to the extent that substantially they pass a 325 mesh sieve.

Preferred anti-agglomeration materials for inclusion in the explosive compositions according to the present invention are those selected from the group consisting of finely divided aluminum, talc, long chain fatty acids such as stearic acid and water soluble salts thereof, and mixtures of these materials.

Our more preferred anti-agglomeration materials are those selected from the group consisting of paint-fine aluminum and a t alc/zinc stearate blend comprising from 90 to 98 parts by weight of talc and from 2 to 10 parts by weight of zinc stearate per 100 parts by weight of blend, and mixtures of these materials.

The amount of anti-agglomeration agent when present which may be used in the coating is not narrowly critical. Suitable amounts are in the range from 1 to 80 parts, preferably from 30 to 70 parts, by weight per 100 parts by weight of the coating.

A further embodiment of our water resistant explosive compositions as hereinbefore described we have found that improved water resistance may result if still further hydrophobic, water repellent or waterproofing agents are incorporated therein. Thus for example we have found it beneficial if in addition to asphalt there is incorporated in our compositions a coating comprising a material selected from the group consisting of paraffin wax and at least one of the so-called drying oils.

By drying oils we mean oily liquid substances that are converted by the action of oxygen or an oxygen containing gas, for example air, to a dry hard insoluble resinous material. The term is typically applied to naturally occurring fatty oils such as linseed, tung, and saflower oils. In the commercial use of these oils it has been found desirable to include therewith small amounts of catalytic materials to increase the rate of hardening and reduce the drying time. Suitable catalytic materials are, for example the oxides, naphthenates, ricinoleates, and linoleates of metals such as manganese, lead and cobalt. For use in the coating materials of the inorganic salt explosive compositions of the present invention a preferred drying oil component is linseed oil with which is incorporated a small quantity of cobalt naphthenate.

Thus in a still further embodiment of our invention we provide explosive compositions of matter as hereinbefore described wherein the coating composition comprises a mixture of asphalt, and finely divided aluminum, optionally in admixture with linseed oil, the proportions of the ingredients may suitably be varied widely. Thus a range of suitable coatings may be prepared wherein the coating comprises asphalt present in an amount in the range from 20 to 99 parts, linseed oil present in an amount in the range from 0 to 40 parts and finely divided aluminum present in an amount in the range from 1 to 80 parts all being by weight per 100 parts by weight of the coating material.

When the coating material comprises a mixture of asphalt, paraffin wax, and a talc/zinc stearate blend as described hereinabove, a range of suitable coatings may be prepared comprising asphalt present in an amount in the range from 15 to 50 parts, paraffin wax present in an amount in the range from 1 to 50 parts, and a talc/zinc stearate blend as defined hereinabove in an amount in the range from 1 to 80 parts, all parts being by weight per 100 parts by weight of the coating material.

The amount of coating which is present in our explosive compositions will depend amongst other things on the nature of the coating material itself and on the surface area of the particles of oxygen releasing salt which it is desired to coat. Thus the smaller the particle size of the oxygen releasing salt, the greater will be the amount of coating material required. The appropriate amount required to coat particles in a specific size range can be determined by simple experiment. In general we have found that explosive compositions comprising from 5 to 25% w/w. of the total composition of coating material are satisfactory and it is preferred that amounts in the range from 5 to 15% w/w. be preferred.

We prefer that the oxygen releasing salt be chosen from the nitrates of the alkali and alkaline earth metals or ammonium and of these we especially prefer sodium nitrate and ammonium nitrate. Ammonium nitrate is particularly preferred. The amount of oxygen releasing salt present in our compositions may be in a range of from 75% to 95% w/w. and amounts from 85% to 95% are preferred. The particle size and shape of the oxygen releasing salt is not narrowly critical and is well known from the art of ammonium nitrate manufacture; powders and ground particles are satisfactory.

It will be appreciated in that the practical usage of explosive compositions it may be desirable to use compositions of differing explosives powers and sensitivities to detonation depending on the application for which an explosive composition is to be used. When desirable therefore it lies within our invention to add to the explosive compositions as hereinbefore described materials which will act as fuel materials and/or sensitizing materials when the explosive composition is detonated. Accordingly in yet another embodiment of our invention we provide an explosive composition as hereinbefore described and comprising in addition at least one material selected from the group consisting of sensitizing materials and fuel materials each as described hereinbelow.

Materials suitable for sensitizing the explosive compositions of our invention are, for example, the self- detonable organic nitro compounds, for example at least one anti-agglomeration agent as hereinbefore defined, preferably a material selected from the group consisting of paint-fine aluminum and a talc/zinc stearate blend, as defined hereinbefore; and thirdly and optionally a material selected from the group consisting of paraffin wax and at least one drying oil, preferably linseed oil.

In the instance where the coating material comprises two or more ingredients the proportion of the individual ingredients in the coating material is not narrowly critical and depends to some extent on the nature of the individual ingredients used in preparing the coating material. Thus for example when the coating material comprises a mixture of asphalt, and finely divided aluminum, optionally in admixture with linseed oil, the proportions of the ingredients may suitably be varied widely. Thus a range of suitable coatings may be prepared wherein the coating comprises asphalt present in an amount in the range from 20 to 99 parts, linseed oil present in an amount in the range from 0 to 40 parts and finely divided aluminum present in an amount in the range from 1 to 80 parts all being by weight per 100 parts by weight of the coating material.

The material thus formed may be shaped or formed into the desired form by in situ reaction in the presence of the coating material described as hereinabove.
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5 erties. Since the inorganic salts often contain absorbed or adhered water, there may be present in our compositions small amounts of water say up to 3% of the weight of the total composition. For certain applications such an amount of water is beneficial; for example in an explosive composition according to our invention the sensitivity to detonation is sometimes enhanced by the presence of such small amounts of water.

10 Where resistive explosive compositions of our invention may conveniently be prepared by first blending the inorganic oxygen releasing salt with a quantity of a substance or a mixture of substances having a hydrophobic or water repellent character, preferably asphalt, in an amount at least sufficient to substantially completely coat the said inorganic salt, and secondly mixing the ingredients for a period of time sufficient to form such a substantially complete coating. Mixing is preferably carried out at ambient temperature although, if desired, elevated temperatures may be used and may be effected by any suitable means known in the art, but it is preferably carried out in a vented tumble-mixer.

15 When the said hydrophobic material is an asphalt it is preferred to add the asphalt as a solution in a liquid aromatic hydrocarbon such as toluene to the inorganic oxygen releasing salt. When desired additional waterproofing agents, such as for example paraffin wax, linseed oil, and anti-agglomeration agents such as a talc/zinc stearate blend or finely divided aluminium powder may be added to the inorganic salt, for example ammonium nitrate, prior to or in admixture with the asphaltic solution, or after the addition of the asphaltic solution.

20 It is preferred that any additional waterproofing agents, when included, be added to the inorganic salt in admixture with the asphalt solution and it is preferred that the anti-agglomeration agent, when included, be added to the inorganic oxygen releasing salt after the mixing step. It is also preferred to include in our compositions sensitizing agents, fuel materials, or other additives, each as described hereinabove, these may be added to the oxygen releasing salt before or after the asphalt solution has been admixed, but it is preferred to add them prior to the addition of the coating materials, especially in the instance where any of the additives is at all water soluble.

25 Accordingly we provide a process for preparing the explosive compositions according to our invention, which process comprises firstly, blending at least one inorganic oxygen releasing salt selected from the group consisting of inorganic nitrates, chlorates and perchlorates, preferably the group consisting of the nitrates of the alkali and alkaline earth metals and ammonium, with a quantity of at least one material comprising a substance having hydrophobic or water-repellent characteristics sufficient to substantially completely coat the said inorganic salt, and secondly mixing the ingredients for a period of time at least sufficient to form such a substantially complete coating.

30 We also provide a process for preparing a preferred explosive composition according to our invention which process comprises firstly blending prilled or granular ammonium nitrate with a substance having hydrophobic or water repellent characteristics, said substance comprising an asphaltic material as defined hereinbefore and optionally a material selected from the group consisting of paraffin wax and linseed oil and present in an amount sufficient to substantially completely coat the said inorganic salt, for a period sufficient to form such a substantially complete coating; secondly and optionally admixing and blending with the coated salt an amount of at least one material selected from the group consisting of additional hydrophobic, water repellent, or waterproofing agents, fuels, sensitizers, and additives as hereinbefore described and blending with the product as formed a quantity of an anti-agglomera-

35 tion agent selected from the group consisting of finely divided aluminium powder and a talc/zinc stearate blend, each as defined hereinbefore.

40 The time required to coat the inorganic salt with the desired coating medium will depend to some extent on the degree of subdivision of the salt and the nature of the coating medium. However in general, coating times ranging from a few minutes to about two hours have been found to be sufficient to provide adequate coatings.

45 The time required to dry the coated inorganic salt also depends on the nature of the coating medium. Thus for example, with certain coatings comprising paraffin wax, air drying at ambient temperature is adequate, while with certain coatings comprising drying oils it may be desirable to heat the coated particles for periods, say up to 24 hours at elevated temperatures, for example between 40 and 70° C, so as to provide a more water resistant coating.

50 Our compositions are advantageous over compositions of the prior art in that they are more resistant to deterioration on contact with water. Our explosive compositions have increased the range of sites at which such explosive compositions may be used and thereby have led to a more efficient and less costly method of blasting in sites where the use of compositions comprising a substantial proportion of inorganic salts has hitherto been impossible due to the presence of small quantities of water at the site of blasting.

55 Accordingly we provide a process of blasting characterized in that the blasting explosive used in said process is an explosive composition according to our invention. We also provide such a process wherein the process is performed at a blasting site in the presence of small quantities of water.

60 Our invention is now illustrated by, but is not limited to, the following examples in which all parts and percentages are on a weight basis unless otherwise specified.

EXAMPLE 1

65 To one hundred parts of “Nitropriil” (“Nitropriil”) is a registered trademark of ICI Australia Limited for a commercially available porous prilled grade of ammonium nitrate) was added ten parts of “Methyl” Grade No. 105/23 (“Methyl” is a registered trademark of Shell Oil Co. Ltd. for commercially available grades of asphalt) and eight parts of toluene, and these ingredients were blended together in a vented tumble mixer for 30 minutes.

70 Mixing was continued at ambient temperature until the coated ammonium nitrate granules just commenced to aggregate and then five parts of “Standard Lining Powder” No. 408 was added ("Standard Lining Powder" No. 408 is a trade name for a grade of paint fine aluminium available commercially from Alcoa Australia Ltd.). Mixing was continued until free flowing coated ammonium nitrate granules were obtained. A 10 g. portion of the product so obtained was stored in 500 ml. of water at room temperature for 20 minutes. After this time the water was separated from the product. Analysis showed that 48% of the ammonium nitrate had been leached from the product. For the purposes of comparison 10 g. of untreated ammonium nitrate prills were added to 500 ml. of water at room temperature. The untreated prills had completely dissolved in the water 5 minutes after being added to the water.

EXAMPLES 2 TO 5 INCLUSIVE

75 In each of Examples 2 to 5 the general procedure of Example 1 was substantially repeated, but in addition in each case 1.5 parts of linseed oil was added concurrently with the addition of the “Methyl.” The general procedure of Example 1 was then again followed to produce water resistant ammonium nitrate compositions according to the present invention.

80 For each of Examples 2 to 5 the ingredients, their amounts in part by weight, and the result of a water
resistance test as described above are listed below in Table 1.

<table>
<thead>
<tr>
<th>Example number</th>
<th>Type</th>
<th>Quantity Type</th>
<th>Ammonium nitrate</th>
<th>Asphalt</th>
<th>Aluminum powder</th>
<th>Waterproof, percent ammonium nitrate leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Nitropill</td>
<td>100 Mephist Grade No. 105/23</td>
<td>5 Standard lining powder No. 408</td>
<td>10</td>
<td>8</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>do</td>
<td>103 Mephist Grade No. 135/7</td>
<td>5</td>
<td>10</td>
<td>8</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>do</td>
<td>100 Mephist Grade No. 135/7</td>
<td>5</td>
<td>10</td>
<td>8</td>
<td>1.5</td>
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<tr>
<td>5</td>
<td>do</td>
<td>100 Mephist Grade No. 135/7</td>
<td>5</td>
<td>10</td>
<td>8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*The free-flowing coated nitrate granules were cured at 54° C, for 16 hours.

**This is a harder grade of asphalt than Grade No. 105/23.

EXAMPLE 6

The general procedure of Example 1 was repeated, except that the 10 parts of "Mephist" Grade No. 105/23 was replaced by 5 parts of "Mephist" Grade No. 135/7, and the 5 parts of "Standard Lining Powder" No. 408 was replaced by 2 parts of vesiculated polyester beads. The polyester beads were prepared from an unsaturated polyester copolymer containing maleic anhydride, phthalic anhydride, and propylene glycol in the mole ratio 1:1:2. 13% of the ammonium nitrate present in the resultant coated particles was leached out by water after immersion in water for 20 minutes.

EXAMPLE 7

The general procedure of Example 1 was repeated except that the 10 parts of "Mephist" Grade No. 105/23 was replaced by 5 parts of "Mephist" Grade No. 135/7 and the 5 parts of "Standard Lining Powder" No. 408 was replaced by 3 parts of "Micafine" P. ("Micafine" P is a trade name for a proprietary brand of leafing grade mica.) 59% of the ammonium nitrate present in the resultant coated particles was leached out by water after immersion in water for 20 minutes.

EXAMPLE 8

To one hundred parts of "Nitropill" was added a blend of 2.5 parts of "Mephist" Grade No. 135/7, 2.5 parts of paraffin wax, and 3.8 parts of toluene and these ingredients were blended together in a vented tumble mixer for 30 minutes. Mixing was continued at ambient temperature until the coated ammonium nitrate granules just commenced to aggregate and then 10 parts of talc/zinc stearate blend comprising 9.5 parts of talc and 0.5 parts of zinc stearate was added. Mixing was continued until free flowing coated ammonium nitrate granules were obtained. The product was then spread on wire trays and allowed to dry for 2 days.

EXAMPLE 9

The general procedure of Example 8 was repeated except that 4 parts of the talc/zinc stearate blend used in that Example were replaced by 4 parts of "Standard Lining Powder" No. 408. There was thus obtained a free flowing explosive composition.

EXAMPLE 10

The general procedure of Example 8 was repeated but the ammonium nitrate of that example was replaced by a blend consisting of 95 parts of ammonium nitrate and 5 parts of sodium nitrate. There was thus obtained a free flowing explosive composition.

EXAMPLE 11

The general procedure of Example 1 was repeated but the amount of "Standard Lining Powder" No. 408 used was increased to 16 parts. There was thus obtained water resistant coated ammonium nitrate granules.

A section of steel pipe 4" in diameter, 30" long, and sealed at one end, was dipped into water and then allowed to stand in a vertical position for five minutes to allow a portion of the residual water on the inner wall of the pipe to drain to the sealed end. To this simulated damp borehole there was slowly added by pouring the explosive composition prepared as described in Example 8 hereinafore, until the pipe was almost filled. Twenty minutes after the composition had been placed in position it was detonated successfully using 142 gm. of pentolite primer.

What is claimed is:

1. A waterproof, free-flowing explosive composition of matter consisting essentially of (1) ammonium nitrate present in an amount from 75 to 95 parts and (2) a hydrophobic coating substantially completely covering said nitrate and present in an amount from 25 to 5 parts by weight per 100 parts by weight of said explosive composition, said coating comprising, on the basis of 100 parts by weight of said coating, from 20 to 99 parts asphalt and from 1 to 80 parts of at least one anti-agglomeration agent.

2. An explosive composition according to Claim 1 wherein said coating comprises asphalt present in said coating in an amount from 30 to 70 parts by weight per 100 parts by weight of said coating.

3. An explosive composition according to Claim 1 wherein said coating also includes linseed oil present in said coating in an amount up to 40 parts by weight per 100 parts by weight of said coating.

4. An explosive composition according to Claim 3 wherein said linseed oil is present in said coating in an amount from 5 to 15 parts by weight per 100 parts by weight of said coating.

5. An explosive composition according to Claim 1 wherein said anti-agglomeration agent is a polyester.

6. An explosive composition according to Claim 5 wherein said anti-agglomeration agent comprises finely divided aluminium.

7. An explosive composition according to Claim 5 wherein said anti-agglomeration agent is a long chain fatty acid or salt thereof.

8. An explosive composition according to Claim 5 wherein said anti-agglomeration agent comprises finely divided aluminium.

9. An explosive composition according to Claim 5 wherein said anti-agglomeration agent is a mixture of from 90 to 98 parts by weight of talc and from 10 to 2 parts by weight of zinc stearate per 100 parts by weight of said mixture.

10. An explosive composition according to Claim 5 wherein said anti-agglomeration agent is a mixture of from 90 to 98 parts by weight of talc and from 10 to 2 parts by weight of zinc stearate per 100 parts by weight of said mixture.

11. A process for preparing the composition of Claim 1 which comprises first blending said nitrate and asphalt until the nitrate is substantially completely coated with said asphalt and then blending the thus coated nitrate with said anti-agglomeration agent until a free-flowing powder is obtained.
12. The process of Claim 11 wherein the nitrate is first blended with a solution of asphalt in toluene.

13. An explosive composition according to Claim 1 consisting essentially of ammonium nitrate, talc, asphalt containing paraffin and finely divided aluminum.

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