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3,014,783

METHOD FOR WATERPROOFING SOLUBLE SALTS AND COMPOSITIONS CONTAINING SUCH SALTS

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This invention relates to new water-resistant compositions and to an improved method for waterproofing the soluble salts used in such compositions as blasting agents, dynamite mixtures and delayed-action fertilizers. More particularly it relates to the development of stable, adherent, waterproof films of grease in situ on the conditioned surface area of discrete particles of a water-soluble salt as ammonium nitrate, sodium nitrate, urea and similar materials commonly used in blasting agents, dynamites and delayed-action fertilizers.

In the waterproofing of commercial explosives, various methods and materials have been used with varying degrees of success. One approach has been to encase dynamite in a water resistance package as waxed paper shells, asphalt-impregnated bags and plastic bags. These packages are readily broken and permit the entrance of water or moisture. Another method has been the incorporation of a water-swelling agent in the formula. Starches, modified starches, starch fractions and certain hydrophilic natural and synthetic compounds have been proposed or used. Many of these form temporary gels; others are too expensive for practical use. Still another method has been the use of water-resistant gelatins. Most common of these is one formed by the combination of nitroglycerine and nitrocellulose. There are many well-known objections to the manufacture and use of these gelatins, such as extreme sensitivity and physiological reactions. Still another method has been the use of water-repellent additives such as oils, greases, waxes, graphites, talcs and various hydrophobic substances, used as internal ingredients in the mixture. Because of the factors which limit the quantity of additive and the mode and temperature of application, none of these has been very satisfactory.

The quantity of oils, greases and waxes which can be added to ammonium nitrate is limited to about 6%. Larger quantities tend to cause a loss in sensitivity to initiation and detonating strength. The addition of any inert material as graphites, talcs, metallic stearates, etc., to an explosive salt, or mixture, results in a corresponding loss of explosive strength. Hence, it is desirable to limit the quantity of such inert additions to about 5%.

Since ammonium and sodium nitrates are powerful oxidizing agents, especially at elevated temperatures, organic coatings are usually applied at less than 212° F., for safety and economy. Unfortunately these temperatures do not reduce the viscosity of the preferred oils, waxes and greases to a sufficient degree to permit adequate coating of discrete particles of soluble salts by available and economic mixing practices. Large areas of surface obviously remain uncoated as shown by the rapidity of solution when salts treated by conventional methods are immersed in water. Hydrophobic powders fail to supply adequate protection for similar reasons, i.e., liquid water is repulsed only in the immediate vi-

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cinity of the hydrophobic particles. Because of their gross size, many surface areas and irregularities on the soluble salt particles are unprotected. Hydrophobic powders leave the soluble salts especially vulnerable to water vapors.

Ammonium nitrate is widely used as the basis of certain types of dynamite. These so-called ammonia dynamites are prepared by mixing special grades of ammonium nitrate, that is finely divided, grained ammonium nitrates, with various other ingredients such as other nitrates, sensitizers such as nitroglycerine, solid fuels and similar materials. Since the ammonium nitrate and other nitrate salts used are water soluble, it has been found necessary to use, as part of the solid fuel, some material which can afford some protection of these salts against penetration by water.

The ammonium nitrate used in fixed explosives has been finely divided ammonium nitrates to provide the required characteristics, as sensitivity and rate of detonation. Coarser grained ammonium nitrate has long been used in fertilizer. Such ammonium nitrates are often in the form of prills, that is, small spherical globules of quite large size compared with the fine particles preferred for explosive powders. Such fertilizer grade ammonium nitrate normally is not useable as an explosive. However, it can be sensitized by the addition of a hydrocarbon such as fuel oil, and when so sensitized can be exploded using a cartridge of dynamite or a package of trinitrotoluene or pentaerythritol tetranitrate as the primer.

Such a mixture of fertilizer grade ammonium nitrate and fuel oil is usually made in the field just before use. One serious deficiency observed in such material is their water sensitivity. Since fertilizer grade ammonium nitrate and prills are usually delivered in 80-pound or 100-pound sacks, it is common practice to pour these materials directly into the borehole either before or after addition of the fuel oil. In wet holes (depending upon quantity of water present) some or all of the ammonium nitrate is immediately dissolved and the oil floated away. Obviously, under these conditions the charge becomes very insensitive.

Since prill-fuel oil mixtures are very economical blasting agents, a method for waterproofing the ammonium nitrate used in such mixtures is highly desirable.

When conditions require specific performance of an explosive, conventional blasting agents can be formulated to deliver the desired results. However, these agents comprise mechanical mixtures of non-explosive oils, greases or finely powdered combustible solids with ammonium nitrate. In some mixtures the oxygen balance is improved by the addition of sodium nitrate or other oxidizing agents. The ammonium nitrate is usually coated with minor additions of anticaking agents as diatomaceous earth and clays or with very minor additions of waxes, greases or resins, or both, to facilitate flow properties during processing and use. Protection afforded by these additions against solution when immersed in water is usually small. Therefore, improved water resistance is also highly desirable for these mixtures.

Many fertilizers also contain ammonium nitrate urea or other nitrate salts. Such salts are quite soluble in water. When such fertilizer is placed upon the ground, a heavy rain or a sudden cloudburst can leach out all

of the nitrate or other soluble salts and wash them from the soil. There is a need in the fertilizer field, for a method of making such soluble nitrates in a form in which it is not apt to dissolve so fast, so as to permit gradual penetration of the soluble salt into the soil where plant roots can get at them. Such a slow dissolution will also permit much larger amounts to be added at any one application, since, slow addition will amount to a series of smaller additions without damage to foliage.

I have now found that ammonium nitrate and similar soluble salts such as sodium nitrate, potassium nitrate, urea and the like can be made with a surprising degree of water resistance. The waterproofed nitrates can be used to good advantage in conventional dynamite or blasting agent formulations. The treated nitrates and urea can be used in delayed-action fertilizers. With proper formulations and treatment, when ammonium nitrate is the principal salt used, the resins and greases which provide water resistance simultaneously sensitize the mixture and, thus, create a safe, economical, water-resistant blasting agent.

The process of my invention consists in coating each particle with a reactive adherent, polar film of a resin which is insoluble in water and grease, converting the film to a metal resinate with a higher melting point than the parent resin, coating the surface of the treated particles with a lubricating oil, and finally, in gelling the oil into a non-tacky grease in situ. Particles of water-soluble nitrates and urea so coated with resins and greases developed in situ have superior resistance to water than that of materials previously used. From 1% to 3% of the coating based on the weight of the soluble salts, applied to the soluble salts in a fertilizer mixture delays solution. From 4% to 8% sensitizes ammonium nitrate and yields a reliable blasting agent for wet or dry work.

The resins which may be used are those harvested from the group of evergreen shrubs and trees commonly called conifers and belonging to the Gymnosperm subdivision of plants. Either the crude rosin gum, the refined wood rosin or a mixture of the two may be used. However, since the crude rosin gum contains a mixture of volatile components which have relatively low flash points, I prefer to use only a small proportion of the crude gum in combination with stearic acid, tall oil pitch, paraffin wax, 12-hydroxystearin, tall oil, etc., as melting point depressants for the wood rosin.

Wood rosin is a solid at room temperature. Temperatures in excess of 230° F. are required to reduce it to a sufficient state of fluidity to coat thoroughly inorganic nitrates. Since they are oxidizing agents, such temperatures are considered unsafe for the coating operation. They are also uneconomical. The use of alcoholic solutions of rosin for coating purposes is also uneconomical. Therefore, I have compounded mixtures of wood rosin, rosin products, stearic acid, etc., which are extremely fluid between 180° F. and 220° F., and which will thoroughly, safely and economically coat inorganic nitrates and urea maintained between 180° F. and 190° F. in a ribbon blender or other suitable mixer. The usage of such modified rosin is from 0.5 to 2.0% of the weight of the soluble salt being coated.

Wood rosin is described in the literature as 60% to 70% abietic, sapinic and pimelic acid anhydrides. By chemical or physical properties unknown to me, wood rosin shows a remarkable affinity for inorganic nitrates. The metal resinates which result when wood rosin and the oxides of barium, strontium and zinc are combined forms a similarly tenacious bond with these salts. The presence of films of grease or wax interfere with the establishment of this cohesive bond between rosin or resinates and inorganic nitrates. Since this bonding action appears to reside in the principal chemical components of wood rosin, I have preferred to use these derivatives of wood rosin (i.e. abietic, sapinic, or pimelic anhydrides or mixtures thereof) and the parent natural gum as the

principal melting point depressants for the applied wood rosin. There should be from 10 to 40% of such depressant added to the rosin.

It should be noted that stearic acid is also an important component of my rosin mixture, since it contributes substantially to the fluidity and chemical reactivity of the resultant melt within the preferred coating temperature range. In turn, it is converted to a useful component, namely, a metal stearate, when the metal oxide is added. This stearate contributes to the development of the final protective film of grease which comprises the last step of my invention. From 5 to 15% of the weight of the rosin mixture, of stearic acid should be used.

Therefore, as the second step in the practice of my invention, I add sufficient (i.e. approximately a stoichiometric amount) of barium, strontium or zinc oxide to convert the rosin to resinates and the stearic acid to stearates. For economy, I prefer zinc oxide. This is added and mixed thoroughly within the preferred temperature range of 180° F. to 190° F.

Likewise, it should be noted that some salts, and especially ammonium nitrate, are subject to severe volumetric changes when crystal inversions occur. Ammonium nitrate passes through two inversions within the preferred temperature range of this invention. At 89.8° F. the volume changes 3.6% and at 183.6° F. a volume change of 1.3% occurs. Such changes tend to fracture any brittle coating which encompasses the individual particles. Wood rosin and metal resinates are brittle substances at normal atmospheric temperatures. Hence, it seems reasonable to assume that fractures and fissures will develop in the resinate films of my invention when coated ammonium nitrate passes through the temperature inversion points noted above.

To prevent ingress of water through any fissures which may develop in the resinate coating, to assure complete coverage of individual particles of the salts and to fill any fissures or other small surface irregularities on the discrete particles of the inorganic nitrates and urea, I have next developed a grease in situ on the coated surface of the discrete particles and within any surface irregularities or fissures as recited above.

To do this, I first add 1% to 8% on the weight basis of the resinate coated material of a normally viscous naphthenic base lubricating oil. This oil is mixed thoroughly with the precoated material within the temperature range 180° F. to 190° F. This addition comprises the third step of my invention.

The oils that I prefer to use are the naphthenic cuts of Mid-Continent and Venezuelan petroleum. In general, the preferred oils are those hydrocarbon petroleum oils normally used to make heavy, stable greases. Such oils should have the following characteristics.

Gravity, ° API	22.0-25.4
Viscosity:	
SSU @ 100° F.	104-1219
SSU @ 210° F.	38.3-78
Viscosity index	26-42
Flash point, ° F.	330-460
SAE viscosity grade	10W-40

The fourth and final step is to add 4% to 8% on the weight basis of the oil of a metal stearate possessing maximum gelling action when heating with viscous, naphthenic base oils. The preferred gelling agents are aluminum salts of fatty acids as described below. Other salts do not seem to operate satisfactorily even though they may be considered equivalent in the grease making art. One important factor is the limited temperature range of this invention, namely 180° F. to 190° F. Normally the gelling temperatures used in making greases are from 250° F. to 300° F. As noted above, these temperatures are above the safe limits for combining nitrate salts and organic materials.

The aluminum stearates which are used in the process of my invention are those especially designed for the

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production of high caliber greases such as are described in United States Letters Patent 2,555,104 to Ashley and Mason and U.S. 2,699,428 to Lux and Parker. Both of these patents describe the formation of aluminum soap combinations for grease making in which at least part of the fatty acid is replaced by a dimer of a drying or semi-drying oil fatty acid. The products produced as special grease-grade aluminum soaps under these patents by the two assignees have been especially found to be usable in the process of my invention. The fatty acids from which the soap is prepared is preferably the stearic acid. One of the best gelling agents which I have found is composed of the aluminum salt of stearic acid mixed with 10% of dimer acid.

It should be stressed that both coatings must be formed in situ. The resinate is formed in this manner because resins are miscible with more economic melting point depressants than are resinates within the temperature limits established. To attain maximum coating of the discrete particles, the very fluid rosin mixture is added first. This point was proven when it was found that adding the zinc oxide first to the heated salts and then adding the rosin mixture resulted in a coating with inferior water resistance. Therefore, the exact order of additions as given must be followed in practicing this invention.

In like manner, better protection is afforded when the oil is added as the third step and permitted to penetrate the surface irregularities of the precoated salts. The metal stearate is added with heat and agitation as the final step to gel the oil to a grease. Inferior water resistance results if this order of addition is reversed and is severely reduced when the grease is produced in a separate vessel and added with mixing to the hot, precoated salts or when the grease is placed on the salt not previously coated with the resinate undercoating. Thus it would appear that a more substantial bond is developed between the resinate and grease when the grease is developed directly on the surface of the resinate. An additional contributing factor may be the formation of grease within the confines of surface fissures and irregularities which are too small for penetration of the finished grease. Cohesive and viscous properties of the grease resist the entrance of water into any subsequent fissures which may develop as the result of temperature inversions in the finished product.

This invention may be practiced in waterproofing soluble salts within the following particle size ranges:

(1) Prilled ammonium nitrate and urea all passing a No. 6 U.S.S. sieve and substantially all retained by a No. 40 U.S.S. sieve, i.e. a range of 420 microns to 3,000 microns.

(2) Grained ammonium, sodium and potassium nitrates all through a No. 8 U.S.S. sieve and substantially 50% retained by a No. 28 U.S.S. sieve. The finest portions of these substances will pass a 200 mesh sieve, i.e. about 74 microns. Thus in summary, the soluble compounds may range in size from 74 to 3,000 microns.

My invention can be illustrated by the following examples in which parts are by weight unless otherwise specified.

Example 1

100 parts of fertilizer grade ammonium nitrate prills of particle size 6-40 mesh is agitated by tumbling in a cylinder which is heated at approximately 180° F. A mixture of 25% crude wood rosin with 75% of a mixture of abietic sapinic and primaric anhydrides extracted from wood rosin is prepared and 1.5 parts of this mixture is then added together with 0.15 part of stearic acid. After 5 to 10 minutes of tumbling 0.3 part of zinc oxide is added. The tumbling is continued and after another 5-10 minutes, 4.0 parts of a naphthenic lubricating oil of SAE 30 grade is added. After another 5-10 minutes of tumbling or when the particles are completely covered, 0.5 part of an aluminum soap of a mixture of 90% stearic acid and 10% dimer acids is added. The tumbling and heating is con-

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tinued until the entire oil coating has been transformed into grease. The mixture is then cooled while continuing the agitation. The product is a water resistant mixture which can be used as a blasting agent. It is found to resist solution and water for as much as ten days of submersion.

Example 2

The procedure of Example 1 is followed using 2.0 parts of the rosin, 0.4 part of zinc oxide, 8 parts of oil and 2.0 parts of the ammonium salt.

Example 3

The procedure of Example 1 is followed using 0.5 part of a mixture of wood rosin with 10% of its weight crude rosin gum, 0.2 part of BaO, 4 parts of oil and 0.25 part of the aluminum soap.

Example 4

The procedure of Example 1 is followed using a mixture of 40 parts of sodium nitrate and 60 parts of ammonium nitrate in place of the ammonium nitrate.

Example 5

The procedure of Example 1 is followed using 100 parts of sodium nitrate in place of the ammonium nitrate.

Example 6

The procedure of Example 1 is followed using 100 parts of potassium nitrate in place of the ammonium nitrate.

Example 7

The procedure of Example 1 is followed using 100 parts of urea prills in place of the ammonium nitrate.

Example 8

The procedure of Example 1 is followed using as the soap, the product of Example 6 of U.S. 2,699,428.

I claim:

1. As a new composition of matter, water soluble compounds selected from the group consisting of urea and a soluble nitrate in the form of small discrete particles, each of said particles being substantially completely covered by a thin film of a metal resinate overlaid with a thin film of a gelled hydrocarbon lubricating oil characterized in that the gelling agent is a member selected from the group consisting of (1) a metal salt of a fatty acid of from eight to twenty two carbon atoms, (2) dimers thereof, and mixtures of (1) and (2), the said metal resinate being a mixture of a salt of wood rosin modified by the addition of 10-40% of a melting point depressant selected from the group consisting of stearic acid, tall oil pitch, paraffin wax, 12-hydroxystearin, tall oil, abietic acid, sapinic acid, pimaric acid, and the anhydrides of said acids, stearic acid being a necessary ingredient used in 5-15% by weight of said metal resinate film, and a metal selected from the group consisting of barium, strontium and zinc, there being present 0.5 to 2.0% of said modified wood rosin based on said water soluble compound, from 1 to 8% of the said gelled hydrocarbon lubricating oil being present, based on the weight of said water soluble compound, said composition being characterized by resistance to dissolution in water.

2. The compositions of claim 1 in which the water-soluble compound is ammonium nitrate.

3. The compositions of claim 2 in which the ammonium nitrate is in the form of a fertilizer grade prills of particle size range 420 microns to 3,000 microns.

4. The process of forming water resistant compositions of water soluble compounds selected from the group consisting of urea and a soluble nitrate in the form of small discrete particles which comprises agitating, said small particles of said compound being between 180° and 190° F., while adding successively (1) from 0.5 to 2.0% of a modified wood rosin containing 10-40% of melting point depressants selected from the group consisting of stearic acid, tall oil pitch, paraffin wax, 12-hydroxystearin,

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tall oil, abietic acid, sapinic acid, pimaric acid, and the anhydrides of said acids, stearic acid being a necessary ingredient used in the range of 5-15% of the weight of said rosin mixture, (2) a substantially stoichiometric amount, based on the acids added in the first step of an oxide of a metal selected from the group consisting of barium, strontium and zinc, (3) from 1-8% based on said water soluble compound of a hydrocarbon lubricating oil, and (4) from 4-8%, based on the oil added in the third step of an aluminum soap of mixed mono and polycarboxylic acids, the proportion of said polycarboxylic acids being from 0.5-25% of the total carboxylic acid and the mono-carboxylic acid being predominantly a fatty acid of 8-22 carbons; each said addition being made only when the said particles of soluble compound is substan-

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tially completely covered with the previously added mixture the agitation being continued after the last mixture until the hydrocarbon film is completely mixed with said soap; and cooling the said mixture.

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