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GRANULAR AMMONIUM NITRATE EXPLOSIVE

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6 Claims. (Cl. 52—21)

The present invention relates to new and improved explosive compositions and methods of manufacturing the same, and, in particular, to a detonating explosive especially desirable for coal blasting.

This application is a division of our co-pending application, Serial No. 269,102, filed April 21, 1939.

The so-called permissible dynamites now in extensive and successful use in the mining of coal represent a marked advance in many respects over black powder, the explosive commonly used in coal blasting prior to the introduction of permissibles. The latter type are detonating explosives and possess the desired safety properties essential when the explosive is to be used in the presence of inflammable mine gases. The permissible explosives are at a disadvantage in one respect, however, when compared with black blasting powder, a deflagrating explosive, in that they do not exert the characteristic sustained heaving action that results with the latter explosive. Consequently, difficulties are met when using permissibles with certain types of coal in obtaining a satisfactory grade of lump coal. A marked advance in the art would be effected if an explosive could be designed which would possess the blasting characteristics of black powder while at the same time representing no backward step with respect to the safety features of the best of the permissibles.

The object of the present invention is an improved explosive composition especially adapted to the mining of coal, said composition having an improved blasting action in this respect over conventional coal mining explosives. A further object is an improved detonating explosive which exhibits a sustained heaving action as contrasted with the shattering action characteristic of explosives adapted to quarry operations, said explosive being characterized by its ability to produce greater yields of lump coal. Another object is an improved detonating explosive which possesses the blasting characteristics of black powder, yet exhibits the safety features of the permissibles. Additional objects will be disclosed as the invention is described more fully hereinafter.

These objects are achieved and the foregoing disadvantages overcome by binding together particles of ammonium nitrate explosive composition into sized aggregates by means of a binding agent substantially insoluble in liquid explosive nitric esters, and coating said sized aggregates with a liquid explosive nitric ester in an amount not exceeding 10% by weight. One preferred product is in the form of grains of such size that substan-

tially all are held on a 30-mesh screen. For instance, highly satisfactory results are obtained from compositions wherein the grains are retained on an 18-mesh screen.

In its most preferred form our invention may be described as a granular powder displaying an apparent density measured by a stick count of from 150 to 215 cartridges of 1½" x 8" in size for 50 lbs. of powder. This same stick count range holds for 1½" x 6" cartridges. Our preferred compositions display a sensitiveness of at least 10" in the half cartridge sensitiveness test, and exhibit velocities below 1450 meters per second. These characteristics are preferred features and are not to be considered as limiting the broad scope of the invention.

In greater detail, we blend a composition comprising ammonium nitrate with a material capable of exerting a wetting action on the surface of the ammonium nitrate particles and other materials present under the influence of a small amount of aqueous solution or other suitable liquid, and of becoming a tenacious solid subsequently, thus functioning as an adhesive to bind the ingredients together. The blended material so constituted is in the form of firm, free-flowing grains of controlled size, and these grains are given a coating of liquid explosive nitric ester in amount sufficient to bring to detonation the entire explosive composition, yet not exceeding 10% by weight.

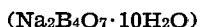
As binding agent or adhesive, we find starch highly effective and advantageous, since, in the presence of water or aqueous solution and under the influence of heat, the starch assumes a gelatinous condition. On subsequent cooling or removal of solvent, the starch becomes hard and tenacious, exerting a firm adhesive effect upon the materials which it has previously contacted. We do not intend to be limited to the use of starch as binding agent, however, and various other materials can be caused to function satisfactorily, for example, agar-agar, casein, animal glue, and the like; in fact, any material capable of becoming mucilaginous and adhering to the solid ingredients present, and of becoming hard and tenacious on cooling or loss of solvent. As already noted, the binding agent must be substantially insoluble in nitroglycerin or other explosive nitric esters in order to be utilizable satisfactorily according to our invention.

Our invention is particularly applicable to explosives high in ammonium nitrate content, for example, between 65 and 80%. The available oxygen present in ammonium nitrate requires the

presence of sufficient oxygen-accepting material, if an effective oxygen-balanced explosive is to result. Starch itself or other organic adhesive may serve this purpose, and we find excellent results to be obtained when an essentially starchy granular material is used, such as a flaked corn product, and when this is properly gelatinized by a small amount of water with heat and is subsequently cooled. We may employ, however, an absorbent, carbonaceous material such as woodpulp, bagasse pith, cornstalk pith, sawdust, and the like, together with an adhesive such as starch. In this latter case, the cells of the absorbent material presumably become filled with the adhesive or the material becomes completely coated therewith.

In order to bring about gelatinization of the adhesive, it is sufficient to wet the surface thereof. This can be accomplished by the direct introduction of water into the mixture of some or all of the ingredients. The presence of an excess of water would defeat the purpose of its use, and we find it desirable to introduce an amount of water not exceeding 5% of the explosive composition, for example, between 1.5 and 3.5%. With such a water content, the starch becomes of mucilaginous consistency on heating, and brings the mixture into plastic form. On cooling, the adhesive becomes hard and tenacious and serves as an effective binding agent.

While the use of water has been described for bringing about gelatinization of the adhesive, other liquids may serve also. We may, for example, employ substantially anhydrous ammonia for this purpose, and in this case heating may be unnecessary, since gelatinization takes place in the cold and the solvent can be readily removed by volatilization. A very effective method also of introducing liquid into the mixture of ingredients is by the employment of salts containing water of crystallization. Hydrated sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$) sodium tetraborate



and the like are examples of such salts, and we find sodium thiosulfate particularly effective for this purpose. In using salts containing water of crystallization, the blend with ammonium nitrate and potential adhesive is heated until the salt melts in its own water of crystallization. Fusion of ammonium nitrate is thereby facilitated, and the liquid present serves to bring about gelatinization of the adhesive. In using salts containing water of crystallization, the water content is desirably controlled in substantially the amount previously stated to be most effective, namely, not over 5% of the entire composition. In place of hydrated salts, we may likewise employ anhydrous salts or salts serving merely as agents to facilitate the fusion of ammonium nitrate, with or without the addition of water to the blend.

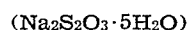
The principle of our invention is to blend together the materials described in the foregoing, form them into granular agglomerates of a controlled size, and then effect proper sensitization. In mixing the ingredients with the addition of heat, a plastic blend is attained. While still in the plastic state, the material is granulated, preferably by passing through a screen of the desired mesh. On cooling, firm, hard grains result and the finished explosive is obtained by introducing sufficient nitroglycerin or other liquid explosive nitric ester to give the desired surface coating.

The use of starch or other nitroglycerin-insoluble adhesive insures that there will be little penetration of the liquid explosive within the grains; hence, increased sensitiveness results with a minimum of liquid explosive. As noted, we find it desirable to use not more than 10% of nitroglycerin, and a favorable amount is between 5 and 8%.

The following will serve as examples of the methods of carrying out our invention and the product obtained thereby.

Example 1

3950 grams of ammonium nitrate, of such a degree of fineness that not more than 20% was held on a 35-mesh screen, was introduced into a mixing apparatus, together with 250 grams of sodium nitrate and 25 grams of calcium carbonate. After agitation had begun, the dry salt mixture was heated to 75° C. by means of steam in the surrounding jacket. 305 grams of hydrated sodium thiosulfate



was then added, followed immediately by 150 grams of starch. Mixing was continued until the starch had become gelatinized and the charge was of such consistency that it resembled bread dough, and remained as a single mass adhering to the revolving mixer blades. 320 grams of bagasse pulp was then added and mixed thoroughly into the blend. The temperature was maintained below 90° C. After addition of the bagasse, the mixture was cooled by means of cold water introduced into the jacket. When the charge had partially cooled but while it was still plastic, it was discharged from the mixer and passed through a 6-mesh screen. After cooling to room temperature, the grains were tough and durable. The material held on a 30-mesh screen was mixed with nitroglycerin in the proportion of 93.5 parts of blend to 6.5 parts of nitroglycerin. When packed in 1½" x 8" cartridges, 167 cartridges per 50 lbs. were obtained. The explosive had a velocity of detonation of 1345 m./sec., and a sensitiveness of 12", as obtained by the propagation test, where two half-sticks of the explosive are separated from one another and the maximum distance of separation is determined at which consistent detonation of the second cartridge by the first takes place.

Example 2

3850 grams of relatively fine ammonium nitrate was introduced into the mixer, along with 500 grams of finely divided sodium nitrate and 25 grams of chalk. The dry mixture was agitated and the temperature raised to around 80° C. by means of steam. 500 grams of a flaked corn product was then added and 125 grams of water. The mixing was continued until the starch had become gelatinized and the proper consistency obtained. The mix was then cooled, screened, and sensitized as in Example 1, 6.5 parts of nitroglycerin being used per 93.5 parts of the salt blend. The finished explosive had a velocity of 1380 m./sec. and a sensitiveness of 10". In preparing the explosive of this example, the flaked corn product used was of the approximate size of granule desired in the sensitized explosive product.

Example 3

3825 grams of ammonium nitrate of relatively fine granulation was introduced into the mixer, 75

together with 500 grams of sodium nitrate and 25 grams of chalk. After agitation had begun, the temperature was raised to about 80° C., and 400 grams of sawdust, 150 grams of starch and 100 grams of water were added. Mixing was continued until the desired gelatinous condition had been obtained on the starch, and the charge had acquired the proper consistency. After partial cooling, the mixture was screened as in Example 1, and the hard grains were sensitized by the addition of nitroglycerin in the amount of 6.5 parts to 93.5 parts of the solid mixture. The cartridge explosive had a velocity of 1316 m./sec. and a sensitiveness of 10''.

Example 4

3875 grams of ammonium nitrate of fine granulation was introduced into the mixer, together with 250 grams of sodium nitrate and 25 grams of calcium carbonate. The mixture was agitated, the temperature was raised to 80° C., and 300 grams of hydrated sodium thiosulfate and 150 grams of starch was added. Agitation was continued to the desired point, and until the charge had acquired the proper consistency. The mixture was screened after partial cooling, as in Example 1, and nitroglycerin was incorporated with the granular material, the amount used being in the ratio of 6.5 parts nitroglycerin to 93.5 parts of the grained material. The explosive after cartridgeing had a velocity of 1085 m./sec., and a sensitiveness of 10''.

Example 5

3925 grams of ammonium nitrate, 250 grams of sodium nitrate and 25 grams of chalk were introduced into the mixing apparatus. During agitation, the temperature of the ingredients was raised by means of steam in the jacket to approximately 85° C. 300 grams of hydrated sodium thiosulfate and 500 grams of a flaked corn product were then added. Mixing was continued until the starch of the flaked corn product had become gelatinized and the proper consistency had been obtained in the charge. The mixture was then cooled somewhat and screened as in Example 1. Nitroglycerin was incorporated with the firm, granular material in an amount corresponding to 6.5 parts nitroglycerin to 93.5 parts of the grains. The cartridge explosive had a velocity of 1320 meters per second and a sensitiveness of 12 to 15''.

From the procedure described in the examples above, and from the discussion of our invention in the foregoing, it will be understood that the invention has to do with explosives high in ammonium nitrate and that various other salts may be present with the ammonium nitrate. Such other salts may include various oxidizing agents, particularly sodium nitrate, though other similar oxygen-carrying salts may be used equally well, for example, potassium nitrate, magnesium nitrate, calcium nitrate, and others. It may be desirable also to use various materials as fusion promoters for the ammonium nitrate, for example, the various hydrated salts, urea, and other materials soluble in molten ammonium nitrate. Such salts and compounds, by promoting the fusion of ammonium nitrate, assist in bringing about the wetting of the surface of the adhesive.

In coal blasting ammonium nitrate explosives of the prior art, it has been the almost invariable custom to employ ammonium nitrate of relatively coarse granulation, since the control of particle size of this explosive salt has been the recog-

nized method for varying detonation velocity. We find, however, that the use of coarse ammonium nitrate is not necessary for making the granular explosive of our invention. Instead we find that the use of relatively fine ammonium nitrate is quite satisfactory for this purpose. For instance, suitable powders according to our invention are prepared with ammonium nitrate of such grain size that at least 40% will pass a 48-mesh screen, while not more than 10% will be held on a 24-mesh screen. This range is satisfactory but not limiting.

As has been stated, our finished explosive is in the form of relatively coarse grains which are firm and free-flowing. While a range of grain size can be employed, we find it preferable that substantially all be held on a 30-mesh screen. In the examples cited, the preferred method of preparing the grains was to screen the blended material while still in plastic condition. Other methods for preparing the grains may be employed, however, such as passing the plastic material into an extruder operated on the meat-chopper principle and extruding through a disc having openings of predetermined size. The method of preparing the grains is not a part of our invention.

It should be emphasized that the material used as adhesive for obtaining a firm, rigid grain must be one which is substantially insoluble in nitroglycerin or other liquid explosive nitric ester. In this way penetration of the liquid explosive into the grain is prevented, and increased sensitiveness thereby results.

The advantage of the product according to our invention lies in the fact that a permissible explosive is obtained of highly attractive properties as a lump coal-getter. In spite of the low velocity, there is no sacrifice in strength or execution. To an unusual degree the slow heaving action of black powder is obtained, with all the safety features of permissible explosives high in ammonium nitrate. Due to the increased sensitizing action of a given amount of nitroglycerin in the explosive composition, a low nitroglycerin content is sufficient to obtain the high degree of sensitiveness previously brought about only by the use of objectionably large amounts of nitroglycerin.

Furthermore, our product possesses marked superiority over explosive compositions of the pulverulent type having approximately the same composition. For instance, comparisons between our granular powders and pulverulent powders having identical low nitroglycerin contents clearly establish that our particular granular compositions display increased propagating ability, lower velocities and improved heaving action in coal blasting.

While our invention has been described in detail in the foregoing, it will be understood that many variations may be made in the exact method of preparation or in compositions without departure from the spirit of the invention. We intend to be limited, therefore, only by the following patent claims.

We claim:

1. The method of preparing a granulated explosive, which method comprises intimately intermingling ammonium nitrate and a material which is substantially insoluble in liquid explosive nitric esters and which is capable of functioning as a tenacious adhesive when subjected to the action of a wetting liquid and subsequently solidified, introducing a relatively small

amount of a wetting liquid into contact with the mixed ingredients, forming the blend of materials, while still plastic, into distinct agglomerates of controlled size, cooling to convert said agglomerates into firm, free-flowing grains, and coating the surface of said grains with a liquid explosive nitric ester.

2. The method of preparing a granulated explosive, which method comprises intimately intermingling ammonium nitrate and a material which is substantially insoluble in liquid explosive nitric esters and which is capable of functioning as a tenacious adhesive when subjected to the action of heat and an aqueous liquid and subsequently solidified, adding a small amount of an aqueous liquid to the mixture and subjecting the blended mixture to the action of heat, forming the blend of materials, while still plastic, into distinct agglomerates of controlled size, cooling to convert said agglomerates into firm, free-flowing grains, and coating the surface of said grains with nitroglycerine in an amount less than 10% of the entire composition.

3. The method of preparing a granulated explosive, which method comprises intimately intermingling ammonium nitrate and starch, introducing into the mixture water in an amount less than 5% of the entire composition, subjecting the mixture to the action of heat, forming the blend of materials, while still plastic, into distinct agglomerates of controlled size, cooling to convert said agglomerates into firm, free-flowing grains, and coating the surface of said grains with nitroglycerin in an amount less than 10% of the entire composition.

4. The method of preparing a granulated explosive, which method comprises intimately intermingling a preponderant amount of ammonium nitrate, starch, a carbonaceous combustible

ingredient, and water in an amount less than 5% of the entire composition, subjecting the mixture to the action of heat, forming the blend of materials, while still plastic, into distinct agglomerates of controlled size, cooling to convert said agglomerates into firm, free-flowing grains, and surface-coating said grains with nitroglycerin in an amount less than 10% of the entire composition.

5. The method of preparing a granular explosive, which method comprises intimately intermingling a preponderant amount of ammonium nitrate, starch, a carbonaceous ingredient, and a salt containing water of crystallization, subjecting the blended mixture to a temperature sufficient to fuse said salt containing water of crystallization, forming the blend of materials into distinct agglomerates of controlled size, cooling to convert said agglomerates into firm, free-flowing grains, and coating the surface of said grains with nitroglycerin in an amount less than 10% of the entire composition.

6. The method of preparing a granular explosive, which method comprises intimately intermingling ammonium nitrate and starch, introducing into the mixture sufficient substantially anhydrous liquid ammonia to effect a gelatinous condition on said starch, forming the blend of materials, while still plastic, into distinct agglomerates of controlled size, cooling to convert said agglomerates into firm, free-flowing grains, and surface-coating said grains with an amount of nitroglycerin sufficient to bring about detonation of the entire composition.

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