

1

3,684,596

PULVERULENT AND WATER BEARING EXPLOSIVE AND PROCESS OF PRODUCING THE SAME

Marcel Vercauteren, Casilla 4244, Lima, Peru
No Drawing, Filed May 1, 1970, Ser. No. 33,901
Claims priority, application Peru, Sept. 15, 1969,
A 8,739/69

Int. Cl. C06b 15/00

U.S. Cl. 149—41

35 Claims

2

ABSTRACT OF THE DISCLOSURE

A pulverulent or water bearing explosive mixture and method of making same comprising mixing 0 to 20% by weight of water, 3 to 6% by weight of liquid hydrocarbons, 50 to 97% by weight of mixed crystals produced by co-crystallization of ammonium nitrate and potassium salts, in a preferred ratio by weight of 20/1 to 4/1, the mixed crystals having a crystal form that is isomorphous with the monoclinic crystal form of ammonium nitrate III, the mixed crystals having a lower temperature of crystal form transition than 32.2° C., which is the normal lower temperature of transition of pure ammonium nitrate III, the mixed crystals being crystallized between 100 and 20° C. in the presence of salts of primary amino alkanes, in the preferred amount of 0.2 to 1.5% by weight, having chain lengths ranging from C₈ to C₁₈, and the mixed crystals having a lipophilic surface characteristic, stable at temperatures below 32.2° C., especially between -20 and +20° C.

The present invention relates to pulverulent and water bearing explosives and processes of producing the same.

In my U.S. Pat. No. 3,499,180, dated June 10, 1969, a process is described in which an ammonium nitrate with lipophilic surface characteristics is used for the fabrication of pulverulent or water-slurried blasting agents. This ammonium nitrate is crystallized between 90 and 20° C. in the presence of 0.2-1.0 percent by weight of salts of primary amino alkanes with a preferable chain length of C₁₂-C₁₄, and in the simultaneous presence of 0.4-1.0 percent by weight of salts of amino alkanols. In this patent, it is expressly stated that to guarantee the lipophilic surface characteristics of this ammonium nitrate at ambient temperature, only the presence of salts of amino alkanols was absolutely necessary; that means that no lipophilic ammonium nitrate is able to exist at ambient temperature, when salts of amino alkanes are exclusively used.

The surface of this ammonium nitrate by adsorption of alkylammonium-micells received the physical characteristic of a hydrocarbon chain, that means a hydrocarbon-loving or lipophilic property, whereby it was made possible that such a surface was able to hold liquid hydrocarbons in a thermodynamic stable manner by adsorption. This special lipophilic characteristic was the starting point for the production of blasting agents with increased detonation sensitivity, brisance and blasting performance.

It always remains a condition precedent that to preserve the lipophilic characteristic only consisted of the combination of amino alkanes-amino alkanols, and that in the absence of amino alkanols, the oil-loving property disappeared rapidly at ambient temperature. During the investigations from which said U.S. Pat. No. 3,499,180 resulted, the function of the amino alkanols was not completely cleared. Experimentally, its essential effect was constantly observed. It was presumed that both amine types were simultaneously adsorbed on the ammonium nitrate surface; also, there existed a suspicion that the adsorbed liquid crystalline layer was composed of an entirely complicated mixture consisting of alkylammonium salts, alkanolammonium salts, water, dissolved ammonium nitrate and other eventually present ions.

Later observations of the explosives according to the above-mentioned patent led to the definite conclusion that the lipophilic characteristic, during cooling, was stable only until about 15° C. in the case of the pulverulent "dry" explosives, and until about 20° C. in case of the water bearing blasting agents. By further falling temperatures, the lipophilic surface characteristic disappeared progressively, which fact can be identified in observing that the compositions began to recrystallize in a very coarse shape, and that the same compositions showed decantations of fuel oil and became insensitive to detonation.

It is an object of the present invention to produce pulverulent or water-slurried explosives, which are also based upon lipophilic crystal surface, but which are capable to keep their oil-loving characteristic down to very low temperatures; which explosives are preferably sensitized by means of liquid hydrocarbons and which do not necessarily require the presence of sensitive and brisant explosives or metallic powders to assure their complete detonation.

The considerations and the steps which led to the present invention may be resumed as follows:

In further connection with the conclusions of said patent, it is reasonable to consider that the voluminous stable adsorbed liquid-crystalline layer will slow down the transformation of crystal state III of the ammonium nitrate to crystal state IV, during cooling. The heat of transition of crystal state III to state IV of ammonium nitrate is exothermic, while the heat of desorption of the micells, as generally known, is always endothermic. According to the absolute values of both these heats, the crystal transformation will only occur partially, i.e. at a lower temperature than 32.2° C., which is the known lower transition temperature of pure ammonium nitrate III. If the absolute value of these heats is the same (or better still, if the absolute value of the positive heat of desorption is higher than the absolute value of the negative heat of crystal transformation), in such a case no transition of crystal form III to crystal form IV should theoretically occur. Nevertheless, it has been experimentally found that the lower transformation temperature of lipophilic ammonium nitrate is displaced highest only until 15° C.

A similar phenomenon is notable at the upper temperature of transition of lipophilic ammonium nitrate, which is displaceable from 84 to 90° C.

It can be experimentally demonstrated that the transformation temperature of lipophilic ammonium nitrate III according to said patent is actually displaced and that the annulation of the lipophilic surface characteristic takes place in the neighborhood of these modified temperatures. This led to the hypothesis that only crystal form III would be capable to adopt a lipophilic surface through adsorption of alkylammonium salts; that this after transition to crystal form IV, which process must be accompanied with a momentaneous desorption of the liquid crystalline layer; this last crystal form IV is not any more suitable for a transition in order to receive hydrocarbon-loving surfaces. As a further deduction, it was set forth that other crystal forms could exist, which external surfaces should have a still more perfect compatibility with the lipophilic adsorbate.

These preliminary ascertainment and hypothesis are the point of departure to the present invention to be described herein below whereby the basic idea consisted in investigating several modifications of the crystal form of ammonium nitrate and its compositions and mixtures with other salts, in order to establish the most favorable crystal form, capable to adopt the most stable lipophilic form.

The general and the patent literature has published a numerous quantity of papers about double salts and mixed

crystals (solid solutions) between ammonium nitrate and other inorganic salts, mainly nitrates. All these double salts and mixed crystals possess exactly defined stabilities at given concentrations and temperatures. Their crystal state is often isomorphous with one of both components, sometimes completely different. The present inventor has prepared a large quantity of double salts and mixed crystals, whereby ammonium nitrate was always the main component. Regarding the double salts, the following cations were tried, whereby the anion was principally maintained unchanged as nitrate and halogenide: sodium, lead (II), lithium, magnesium, calcium, uranyl, thorium (IV), etc. Solid solutions in ammonium nitrate were prepared with the nitrates, halogenides, acetates, etc. of the following best-known cations: potassium, rubidium, caesium, thallium (II).

From all tests with double salts, it appeared that none of the examined combinations showed a lipophilic surface characteristic in presence of salts of 1-amino alkanes. In certain cases, especially the double salts with magnesium nitrate, a real retrogradation or deterioration of the lipophilic property with respect to pure ammonium nitrate was verified.

Comparatively, the mixed crystals have the advantage that relatively low quantities of incorporated salts are sufficient to provoke important modifications of the crystal state. Solid solutions in very different proportions have been prepared, without success, with the nitrates, halogenides and organic salts of rubidium, caesium and thallium (II). It is to be observed that all the crystal forms of these mixed crystals, according to the respective concentrations, are either isomorphous with the corresponding Rb, Cs and Tl (II) -salts, or isomorphous with the modifications II and IV of ammonium nitrate; or, however, belong to completely different crystallization systems. The same observation is also valid for the case of the above considered double salts.

Only the mixed crystals between ammonium nitrate and potassium salts, preferably potassium nitrate, show a lipophilic surface characteristic in the presence of alkylammonium salts. These mixed crystals are also the only ones, whose crystal form at ambient temperature or at a lower temperature is isomorphous with ammonium nitrate III.

The reasons why the monoclinic crystal form of ammonium nitrate III and the isomorphous crystal form of its solid solutions with potassium nitrate are the only ones which are appropriate to get a lipophilic surface characteristic, are according to the inventor's observations, the following:

(1) The alkylammonium-ions exist within a saturated ammonium-plus-potassium nitrate solution in the form of very highly associated micells, in equilibrium with the total electrolyte solution. Furthermore, an eventual excess of alkylammonium-ions exists as highly concentrated micells, in equilibrium with the smallest quantities of the total electrolyte solution. The former alkylammonium-micells have to be considered as "soluble" and the latter as "insoluble." Following modern theories, the dissolved micells have a "lamellar" configuration, in which each single alkylammonium-ion is disposed almost in parallel with respect to the other ions, in one or several layers; they simulate a crystalline-like structure in one plane and have a more or less pronounced disorder in the third dimension. These micells will be adsorbed in a most stable manner on such crystals which have an extended and smooth surface of similar or nearly similar dimensions as the crystal-like surface of these micells. The needle-shaped acicular ammonium nitrate III and the modification which is provoked by the presence of potassium nitrate should comply with these conditions.

(2) Only in very concentrated electrolyte solutions the alkyl-ammonium salts are able to exist under form of soluble micells, this being an absolute necessity for the instantaneous formation of an adsorbate on the crystalliz-

ing mixed crystals. Saturated solutions between ammonium- and potassium-nitrate fulfill this condition.

To obtain the mixed crystals, almost all potassium salts are applicable, especially in water containing explosive compositions, where a metathetic reaction is quite feasible with formation of potassium nitrate. Potassium salts, whose anions can have an unfavorable reaction with the alkylammonium-cation, must, of course, be excluded. To this group belong, for instance, potassium sulfocyanide (alkylammonium-sulfocyanide forms an insoluble liquid coacervate), potassium sulfate (alkylammonium sulfate has a much too low solubility), etc. Other potassium salts are applicable, but in certain cases not recommended; to that belong, for instance, potassium acetate (potassium acetate increases the pH of ammonium nitrate solutions, which causes a decrease of the solubility of the alkylammonium salts), potassium chloride and potassium fluoride (these salts may contract ternary and quaternary mixed crystals with ammonium nitrate, which are isomorphous with ammonium nitrate III, but whose crystals may have certain modified faces which are less suitable for a most stable adsorption of the micells).

The preferred potassium salt in the compositions according to the invention is potassium nitrate, because the presence of an excess of foreign-ions influences more or less the perfect crystal form of the pair ammonium nitrate-potassium nitrate.

The preferred percentage of potassium nitrate or other potassium salts lies at about 7%. The practical advantageous percentage fluctuates between 3 and 15% or, in other words, the ratio by weight ammonium nitrate/potassium nitrate should lie between the values of 20/1 and 4/1. By all means, higher amounts of potassium salts are, of course, applicable but not justified for the desired purpose. Lower quantities than 3% could be applied in cases where the temperature of storage and surroundings of the explosives should always remain relatively elevated.

The alkylammonium salts must be present under the most convenient form possible, in order to attain a most dense and stable adsorbate. As previously mentioned, the soluble alkylammonium salts are the ones which form the lipophilic micell layer on the mixed crystals; therefore, it is important to choose a sufficiently soluble salt avoiding, nevertheless, the use of an excessively soluble salt which would retrograde the maximum adsorption. Further on, a certain excess of undissolved alkylammonium salts (generally in the state of a gel) must always be present; in other words, a saturated solution of alkylammonium micells must constantly be provided. Under such circumstances, a spontaneous adsorption takes place on the surface of the mixed crystals, in which process the insoluble alkylammonium salt serves as a reservoir to compensate continuously the saturation of the soluble micellar phase. Pure n-octylammonium- and pure n-decylammonium-salts are not advantageously useable, due to their excessively high solubility; n-dodecylammonium salts approach a favorable solubility limit; higher alkylammonium salts possess a much too low solubility. In most cases, mixtures between C₁₂, C₁₀ and C₈-alkylamines are selected to attain the desired solubility. A mixture consisting of C₈ to C₁₈ n-alkylamines, commercially known as "coco-amine," is also advantageously admixable.

The choice of the anion of the alkylammonium salts varies accordingly to the desired explosive type and/or sensitivity of detonation. In water bearing blasting agents the monovalent anions of the strongest inorganic acids are preferred, in the following order: perchlorate, chloride, nitrate. This order is in correspondence with the decreasing degree of dissociation of the respective acids. This phenomenon is explained as follows: The higher the degree of ionization of the alkylammonium salts, the harder will be the salting out through flocculation of the same in presence of an excess of electrolytes. In this way, it appears that the n-alkylammonium perchlorate micells are the most soluble, and that the n-alkylammonium-nitrate micells are the less soluble in this considered series,

wherefore the former will produce the most sensitive water containing blasting agents. This can experimentally be verified by means of the determination of the critical diameters for complete detonation of equivalent water containing blasting agents, in which only the anion of the alkylammonium salt has been varied: In case of perchlorate, the critical diameters lie at about 2 to 2.5 inches (50–62.5 mm.); for chlorides, i.e. the critical diameters increase up to 2.5 to 3.5 inches (62.5–87.5 mm.); and when nitrates are set in, critical diameters stabilize at values of 3 to 4 inches (75–100 mm.). In pulverulent explosives, inorganic or organic best soluble alkylammonium salts are preferred, in such a way that the pH of the surrounding solution of the lipophilic mixed crystals is not higher in the finished product than the pH of pure ammonium-plus-potassium nitrate solutions, i.e. at about 6, since the free H⁺-ions have a strong flocculating effect on the n-alkylammonium micells. Thus, if in this case inorganic salts are chosen, these should be formed in situ by means of acid salts, preferably zinc nitrate.

The preferred percentages of alkylammonium salts in the explosive mixtures fluctuate between 0.2 and 1.5%. Amounts higher than 1.5% are of no essential advantage. Lower quantities than 0.2% are not able to guarantee a sufficient "lipophilization" of the surface of the mixed crystals.

According to experience, it has been established that the most stable lipophilic surface of the mixed crystals comprises n-dodecylammonium salts, wherefore this amine will appear in all compositions, but seldom as the only one. Besides of the particularity to have guaranteed a monoclinic crystal surface, stable at low temperatures, by means of the salt pair ammonium nitrate-potassium nitrate, it appears that the solubility of the amines at these same low temperatures must also be kept always sufficiently high, preferably higher than the critical concentration for micell formation. This is attained by mixing n-dodecylamine with the lower C₈ and C₁₀ amines, which makes it simultaneously possible to lower the Krafft-temperature (temperature at which the critical concentration for micell formation commences), desirably to below 0° C.

Regarding the range of the higher temperatures, it is demonstrated that starting from 60–65° C. the solubility of the n-dodecylammonium salts (pure or mixed with the lower alkylammonium salts) commence to strongly increase in such a way that the affinity of the micells is displaced towards the aqueous phase, and that a great diminution of the aggregation number becomes noticeable. This disadvantage is reduced or eliminated when the temperature of crystallization of the mixed crystals is lowered through addition of inorganic salts or organic substances. Sodium nitrate and calcium nitrate count among the most important and best-known substances which have the aforementioned property to increase the general salt solubility. By increasing the water contents of the pure ammonium-plus-potassium nitrate solution, the same effect is attained, but such an increase of the water contents for blasting in technical output reasons is many times not desirable. The preferred contents of these inorganic salts, which are able to increase the general solubility of the electrolytes, at constant water contents, lies between 4 and 8% by weight, which the water bearing slurried blasting agents concerns. For the production of the pulverulent explosives this first kind of salts, which enables the aforementioned increase of solubility, is preferably not used.

A second group of substances, which are capable of increasing still more the sensitivity of detonation of the water containing blasting agents, are such organic liquids, which are simultaneous solvents for alkylammonium salts and ammonium-plus-potassium nitrate. It has been found that formamide is the most important of these substances. It is remarkable that a 12.5 molal solution of ammonium nitrate in pure formamide, at 20° C., does not have a flocculating action upon simultaneously dissolved n-dode-

cyammonium-chloride, whereas, to the contrary, a 0.1 molal aqueous solution of ammonium nitrate has already a salting-out effect. Furthermore, it is to be mentioned that this great increase of solubility of the n-dodecylammonium salts does not cause a diminution of the micell aggregation number. Both of these factors contribute to assure a better "lipophilization" of the mixed crystals, by which mechanism it is made possible to produce water containing blasting agents, the critical diameter of which can be set down until 1.5 inches (37.5 mm.) and the minimum booster weight (initial explosive quantity) of which can be lowered until 1/2 lb. (38 gr.); (still further reduced diameters and smaller booster weights were not tested due to practical field execution reasons). Other organic substances, inclusive of crystallized compounds, have a similar effect as formamide; among them may be considered principally glycol and glycerine, dimethylformamide, urea, etc. Nevertheless, formamide is by far preferred, which, as heretofore explained, has the property of increasing the solubility of the alkylammonium salts in saturated electrolyte solutions at low temperatures.

The very water soluble alkanolammonium salts, specially triethanolammonium nitrate and triethanolammonium acetate, which is a highly viscous fluid at room temperature, also belong to this group. Because of their ionic character, these salts will have their greatest efficiency as solvents for alkylammonium salts only in media of very low water contents. Therefore, the lower alkanol ammonium salts with alkyl chains of preferably 2 or 3 carbons find their application in the pulverulent explosives of the present invention.

The preferred contents of these compounds, which increase the solubility of the alkylammonium salts without decreasing the aggregation number of the micells, lies between 1 and 2% by weight, in case of the pulverulent explosives, and between 5 and 7% by weight, in case it concerns water containing slurried blasting agents.

It follows from the foregoing exposition that the most important secondary component of the water bearing blasting agents according to the invention is formamide, because it produces simultaneously a descent of the saturation temperature of the hot ammonium-plus-potassium nitrate solution and an increase of the solubility of the alkylammonium salts at the lower temperatures, without provoking a degradation of the micellar complexes. Within the same development it must be further remarked that the secondary components of the first group, such as sodium nitrate and calcium nitrate, have also a certain solubility regulating function with respect to the alkylammonium micells at the low temperatures, since the solubility of the micells augments with increasing molality of the dissolved inorganic salts. The auxiliary components of the before considered first and second group have also a solubility regulating function, though in a lesser degree, at the low and high temperatures, respectively. In summary, the progress of the herein described invention comprises mainly, firstly, in the fact of substituting in the water containing slurried blasting agents for the alkanolammonium salts, which was proposed in my U.S. Pat. No. 3,449,180 by formamide or similar acting substances; and, as well as, secondly, in the novelty of making use of lipophilic mixed crystals instead of lipophilic ammonium nitrate, due to which it is not absolutely necessary to execute the crystallization of the lipophilic mixed crystals in the simultaneous presence of alkylammonium salts and of alkanolammonium salts or other alkylamine solubility increasing substances, in order to maintain the lipophilic surface characteristic at low temperatures. Nevertheless, as is to be understood from the foregoing exposure, the simultaneous use of 1-amino alkanes and of the formerly defined substances is a preferred practice.

It should be observed here that such components as sodium nitrate, formamide, urea, etc. also appear in the composition of many conventional explosives (water

bearing or not), wherefore the peculiar stabilization effect of these substances must be accentuated in the compositions according to the invention. Particularly formamide has already been proposed for use in water slurried blasting agents, in order to attain or to improve the following characteristics: as a means to depress the freezing point; as a means to increase the energy and sensitivity of the aqueous phase; as a dispersion- or solvent-medium for certain present components, such as, for instance, nitro-compounds. According to the foregoing description, it could be expressed that formamide in the compositions according to the invention sensibilizes indirectly the crystalline phase, because by an increase of the solubility of the n-alkylammonium micells, the lipophilic characteristic of the crystalline phase is reinforced. Furthermore, it results from examples 6.3.1 to 6.3.9, herein, that formamide has its maximum effect only within a narrow concentration range. At lower or higher concentrations than the optimum ones, the sensitivity of the corresponding explosive mixtures suffers a rapid retrogression, because the solubility of the n-alkylammonium micells in the respective solutions has not yet reached or already surpassed its optimum value. The optimum ratio by weight of water/formamide lies between 2.5/1 and 3.5/1.

Other water soluble combustible materials are not recommended to be used in the compositions according to the present invention. Methanol and ethanol have a solubility-increasing effect on the alkylammonium salts, however with simultaneous and rapid reduction or of the aggregation number of the micells complexes.

Other additional components of these explosive mixtures are: barium nitrate, mostly up to 0.5%, to participate the disturbing polyvalent anions; zinc nitrate, up to 1% as pH regulator, if necessary, etc. Metallic powders, principally aluminum, may be admixed in a desired quantity in order to increase strength and brisance of the explosive mixtures. Water-swelling polymers are used to obtain the water resistance of the slurries. The chosen swelling polymers must be of non-ionic nature, or else a reaction occurs with the alkylammonium ions with loss of the lipophilic property of the mixed crystals. Guar flour and polyacrylamide were found to be the best appropriate swelling compounds; on the contrary, the anionic carboxymethylcellulose, for instance, is by no means applicable. It appears that all incompatibilities between undesired impurities and the alkylammonium salts must be avoided. Such impurities consist in the first place of almost all polyvalent anions and are often carried along with the used raw materials. For instance, Chile saltpeter contains, among other impurities, about 0.5% sulfate ions. Likely, certain ammonium nitrate qualities may contain 0.1 to 0.3% sulfate ions; especially prepared qualities of guar flour may hold varying percentages of borate-, chromate-, antimoniato- etc. ions. Such guar qualities should not be used; the use of guar flour should be limited to the "pure" quality or to the so-called self-complexing kind. The formerly mentioned sulfate ions can generally not be avoided; they are easy to eliminate through addition of an equivalent quantity of a barium salt, which precipitates at the same time most of the other polyvalent anions. Certain technical ammonium nitrate qualities contain surface active substances used as anticaking agents. The use of such an ammonium nitrate should be avoided, even if the surface active anti-caking agent is a primary aliphatic amine, in order to not originate uncontrollable interferences. If the anti-caking agent would be of an anionic nature, in that case the use of a so treated ammonium nitrate is absolutely prohibitive. The same observation holds for sodium- and potassium-nitrate. The higher aliphatic alcohols, starting from propanol, provoke a complete decantation of the alkylammonium salts as liquid coacervates, and the higher aliphatic acids combine as unsoluble compounds. To produce the lipophilic mixed crystals it is parted from a hot solution, which is mostly saturated at a temperature of 60 to 100° C. At a tempera-

ture higher than 100° C., imperfect lipophilic mixed crystals are obtained or none at all, for the same reason as has been explained herein in the introduction: Subject to the contents of potassium nitrate and at temperatures above 84° C., which is the established upper temperature of transition of crystal form III of pure ammonium nitrate, mixed crystals are still obtained, which are isomorphous with ammonium nitrate III; at still higher temperatures and subject to the potassium nitrate contents, a non-lipophilic crystal form, isomorphous with ammonium nitrate II or with potassium nitrate, is formed; above 110° C. no lipophilic crystals will form anymore. Preferably a maximum temperature of 100° C. should not be exceeded in production processes of "dry" pulverulent explosives. In production processes of water containing blasting agents, a maximum starting temperature of 60 to 65° C. is recommended.

The hot starting solutions for crystallization comprises water, ammonium nitrate, potassium nitrate, eventually alkaline or earth-alkaline nitrates, formamide or other water soluble facultative components and alkylammonium salts (as such as salified in situ). The crystallization of the lipophilic mixed crystals can be carried out by means of generally known devices and methods; in spite of the fact that an evaporation of saturated solutions at constant temperature and at sub-atmospheric pressure is preferred. It is not indispensable to produce completely dry mixed crystals; a remaining humidity of 1-2% does not unfavourably affect the quality of the corresponding pulverulent explosives.

The composition of the lipophilic mixed crystals lies preferably within the following limits: 82 to 95% by weight of ammonium nitrate; 3 to 15% by weight of potassium nitrate; 0.2 to 0.5% by weight of alkylammonium salts; and, 1 to 2% by weight of triethanolammonium salts, with a final humidity of 0.2 to 1% by weight.

As a sensitizer of the lipophilic mixed crystals, the commercially available derivatives of mineral oil are preferred, principally fuel oil. The chain length of the preferred hydrocarbons comprises about 12 carbons. Linear or ramified aliphatic hydrocarbons, as well as cyclic or aromatic hydrocarbons are equally applicable.

Brisant high explosives, such as nitroglycerine, trinitrotoluene, starch-nitrate, pentaerythrite-tetranitrate, sugar-nitrates, etc. may also be admixed in desired amounts. Nevertheless, in this invention their traditional functional as a sensitizer has been substituted by the lipophilic mixed crystals, which makes their presence not absolutely necessary. As a further object the present invention consists in producing economical and safe-to-handle explosives, the application of brisant high explosives is not recommended. In the same way, metallic powders, principally aluminum powder, is not necessary to sensitize the explosive mixtures. Nevertheless, these metallic powders are advantageously admixed to increase strength and brisance in cases where such an increase is desired.

The preferred pulverulent explosive mixtures consist mostly of 84 to 97% by weight of lipophilic mixed crystals, 3 to 6% by weight of diesel oil (fuel oil No. 4, according to the American ASTM classification) and 0 to 15% by weight of metallic powders, preferably aluminum. These pulverulent explosives are of extraordinary strength and brisance; they may be packed in cartridges of small diameters, e.g. 7/8 inch (72 mm.), and they are sensitive to detonation with a blasting cap No. 6. The manner of handling of the cartridges is not different from the conventional ammoniacal dynamites. The pulverulent explosives, according to the present invention, may also be packed in bags in order to be poured loose into the bore holes.

The slurried water containing explosives may be produced in two different ways: Firstly, use can be made of the "dry" lipophilic mixed crystals, as formerly described, which are introduced in an at room temperature saturated electrolyte solution, together with diesel oil and

other desired components. The electrolyte solution should at least contain ammonium nitrate, a potassium salt, and an alkylammonium salt; other desired soluble secondary components may be added. Nevertheless, the preferred method to produce the slurries comprises simply in cooling a hot saturated solution down to 20–30° C., whereafter diesel oil, guar flour, aluminum powder, etc. are admixed, without separating the mother liquor.

The preferred compositions of water bearing slurried blasting agents fluctuate mostly within following limits (all percents are percents by weight): 12 to 20% of water; 50 to 70% of ammonium nitrate; 3 to 15% of potassium nitrate (or partially another potassium salt); 4 to 15% of secondary substance (being the sum of sodium nitrate, calcium nitrate, barium nitrate, formamide, urea, etc.); 0.4 to 1.5% of alkylammonium salts; 0 to 20% of aluminum powder (or another metallic powder); 3 to 6% of diesel oil (fuel oil No. 2 according to the American ASTM classification); and, 0 to 0.7% of a water swelling colloid or polymer (guar flour or polyacrylamide). In certain compositions small amounts of other combustible materials are also admixed, such as carbon, asphalt powder, etc. Brisant high explosives are, of course, also applicable; nevertheless (as in the case of the pulverulent explosives) they are not necessary to sensitize the blasting agent.

The water containing blasting agents are packed in plastic bags or may be directly bulk loaded in the drill holes by means of a delivery truck. The advantages of these new slurries consist in an excellent sensitivity to detonation in small diameters (bore holes), and in the need of but a very small booster weight (initial explosive quantity) for their complete detonation. Detonation sensitivity is insured down to a critical cartridge—or bore hole diameter of 1.5 inches (37.5 mm.) in case of special compositions as described above, and up to the critical loading density of 1.55 gr./cm.³. Comparatively, these figures reach the values of 5 inches (125 mm.), respectively, 1.20 gr./cm.³, for the slurries of U.S. Pat. No. 3,449,180. A further characteristic of the slurries according to the present invention concerns their unusual air gap sensitivity, which can go up to 12 inches (30 cm.) for charges of 6.5 inches (162.5 mm.) diameter loadings. These characteristics, which have not yet been known, are the best insurance for a complete detonation of these new water containing blasting agents.

Finally, it must again be emphasized that the slurries according to the invention are fully usable at very low field or operating temperatures, beneath 0° C., which was until now very problematic for what the slurries of the prior art concerns, inclusive of such slurries which are sensitized by means of brisant explosives. In this connection it is to be observed that the water bearing explosives according to the present invention begin to lose their fluidity at 10° C. and that beneath 0° C. they transform in tough semi-solid masses, which makes difficult the loading operation in the bore holes. For this reason and in case of very low field temperatures, the use of a de-

livery truck is recommended to pump the fresh explosive with a temperature of 20–30° C. into the bore holes. A subsequent solidification of the explosive within the bore hole is of no importance.

By means of the following examples the invention will be exemplified: Examples 1 to 4 illustrate the theoretical basis of the invention. Example 5 describes a few typical methods of preparation of water containing explosives according to the invention; and Example 6 resumes the characteristics of same. Example 7 gives a few methods to prepare lipophilic mixed crystals which can be used as raw materials for the elaboration of the pulverulent explosives of Example 8.

EXAMPLE 1

The solid solutions between potassium nitrate and ammonium nitrate have been principally and intensively investigated by Prof. Dr. E. Jaenecke of the former "I. G. Farbenindustrie A.G." (Germany). Several compositions of mixed crystals have been repeated by the inventor with the variation that crystallization was carried out in presence of n-alkylammonium chloride. The percentage of n-dodecylammonium chloride plus n-octylammonium chloride was kept constant at 0.5 g. in all preparations, wherein the reciprocal proportion between C₁₂ and C₈ was constantly decreased with falling temperature according to the conclusions of Example 3. In all preparations, the quantity of water and of ammonium nitrate was kept constant at 15, and 66 g., respectively. In Example 1.1, the variation consists in adding varying quantities of potassium nitrate; in Example 1.2, varying amounts of potassium- and sodium-nitrate were applied. In each case a saturated solution was prepared at 60 to 70° C., which was subsequently cooled under agitation by hand, in tap water, down to 30° C., whereafter, and without separation of the mother liquor, the samples were stored during 48 hours at varying temperatures. The progressively changing temperatures were of 20, 15, 10, 5, 0, –5, –10, –15, and –20° C. One and the same sample was exposed to a gradually descending temperature, until a "de-lipophilization" of the crystals could be verified, which in the present case was easy to demonstrate by the fact of a modification of the crystal size towards a coarse unevenly shaped form (microscopically or, in many typical cases, visually appreciable). An additional method to recognize the "de-lipophilization" comprises mixing the presumably transformed crystal mass (plus mother liquor) with fuel oil, whereby a rapid decantation of the oil is observable. Before transformation of the crystals takes place, it is clear that no oil decantation occurs. The "de-lipophilization" of the mixed crystals cannot sharply be established but appears progressively. In the following tables two different temperatures are considered: T₁=upper temperature, at which a "de-lipophilization" is not yet observable; T₂=lower temperature, at which no lipophilic mixed crystals are present anymore. The difference between T₁ and T₂ is kept constant at 5° C.

EXAMPLE 1.1

Preparation No.	Composition of solution (g.)					
	H ₂ O	NH ₄ NO ₃	C ₁₂ H ₂₅ NH ₃ Cl/ C ₈ H ₁₇ NH ₃ Cl	KNO ₃	T ₁ (° C.)	T ₂ (° C.)
1.1.1.....	15	66	0.5	0	-----	20
1.1.2.....	15	66	0.5	1.5	-----	20
1.1.3.....	15	66	0.5	2.25	-----	20
1.1.4.....	15	66	0.5	3.0	20	15
1.1.5.....	15	66	0.5	3.75	20	15
1.1.6.....	15	66	0.5	4.5	15	10
1.1.7.....	15	66	0.5	5.25	15	10
1.1.8.....	15	66	0.5	6.0	10	5
1.1.9.....	15	66	0.5	6.75	5	0
1.1.10.....	15	66	0.5	7.5	5	0
1.1.11.....	15	66	0.5	9.0	0	–5
1.1.12.....	15	66	0.5	10.5	–5	–10
1.1.13.....	15	66	0.5	12.0	–5	–10
1.1.14.....	15	66	0.5	13.5	–10	–15
1.1.15.....	15	66	0.5	15.0	–10	–15
1.1.16.....	15	66	0.5	16.5	–15	–20

EXAMPLE 1.2

Preparation No.	Composition of solution (g.)					T ₁ (° C.)	T ₂ (° C.)
	H ₂ O	NH ₄ NO ₃	C ₁₂ H ₂₅ NH ₃ Cl/ C ₈ H ₁₇ NH ₃ Cl	KNO ₃	NaNO ₃		
1.2.1	15	66	0.5	0	12.5	20	
1.2.2	15	66	0.5	1.5	10.5	20	
1.2.3	15	66	0.5	3.0	9.0	20	
1.2.4	15	66	0.5	4.5	7.5	15	
1.2.5	15	66	0.5	6.0	6.0	5	
1.2.6	15	66	0.5	7.5	4.5	0	
1.2.7	15	66	0.5	9.0	3.0	-5	
1.2.8	15	66	0.5	10.5	1.5	-10	

It is interesting to notice how the temperatures of "de-lipophilization" of the foregoing tables approach Dr. Jaenecke's temperatures of crystal transition, which proves that only a crystal form, which is isomorphous with the monoclinic ammonium nitrate III, is able to adopt a lipophilic surface characteristic by means of absorption of alkylammonium micells.

EXAMPLE 2

Again a certain number of solutions is prepared consisting of 15 g. of water, 66 g. of ammonium nitrate, 0.5 g. of n-dodecylammonium-chloride plus-n-octylammonium-chloride and 4.5 g. of a varying potassium salt according to the following table. Each saturated solution is cooled down to 30° C., whereafter each sample is exposed to the progressively varying temperature cycle, as in Example 1, in order to determine in each case the temperatures T₁ and T₂.

Potassium salt	T ₁ (° C.)	T ₂ (° C.)
Potassium nitrate	15	10
Potassium fluoride	0	-5
Potassium chloride	10	5
Potassium bromide	15	10
Potassium iodide	20	15
Potassium formate	10	5
Potassium acetate	15	10
Potassium citrate	15	10
Potassium oxalate	15	10
Potassium bichromate	20	15

Comparatively with Example 1, higher or lower "temperatures of de-lipophilization" are found for the foregoing preparations; for the case of the higher temperatures the reason is to be found in the fact that the considered anion diminishes excessively the solubility or provokes the complete precipitation of the n-alkylammonium-cation, notwithstanding that a crystal form transition of the mixed crystals has not yet necessarily taken place. Regarding the lower temperatures, the explanation is more complicated: The presence of certain anions (chloride, fluoride) facilitates the formation of ternary or quaternary mixed crystals, which are also isomorphous with the crystal form of ammonium nitrate III, but which has a still lower transition temperature. Nevertheless, this isomorphism may have unfavorable undefined forms, from which certain disadvantages, in contrast with potassium nitrate, may result.

EXAMPLE 3

Several simultaneously saturated solutions consisting of ammonium nitrate, sodium nitrate, and potassium nitrate are prepared at temperatures of 30, 20, 10, 0, -10° C. To each sample, which contains 15 g. of water, 0.5% by weight of n-alkylammonium-chloride is added, whereby the relation between C₁₂ and C₈ is changed. All samples are stored in a thermostatic chamber, where temperature is progressively regulated at 30, 20, 10, 0, and -10° C. The samples are observed after each course of 2 hours. In case a crystallization of mixed crystals occurs, before a flocculation or a crystallization of the n-alkylammonium salts takes place, the respective samples are eliminated and substituted by other ones, the saturation temperature of the inorganic salts of which is a lower one. At the occasion of each check at a defined cooling temperature, all such samples are removed

which show a flocculation or a crystallization of the n-alkylammonium salts. The solutions are slowly warmed up again under constant and intensive agitation with a thermometer, during which operation a gradual re-dissolution of the precipitated matter is visible. The temperature at which a complete dissolution occurs is checked (a slight residual turbidity is almost always visible, which is originated by a separate gelatinous phase). In this way the temperature of saturation of the co-dissolved n-alkylammonium salts is established as follows:

No.	Proportion by weight of C ₁₂ H ₂₅ NH ₃ Cl/ C ₈ H ₁₇ NH ₃ Cl	Temperature of saturation, ±1° C.
3.1	10/0	28
3.2	9/1	20
3.3	8/2	16
3.4	7/3	12
3.5	6/4	8
3.6	5/5	3
3.7	4/6	0
3.8	3/7	-3

For each considered case it has been determined in this example the temperature at which a decrease of solubility of the n-alkylammonium salts begins. Other similar series may be executed, in which the nature and the amount of the n-alkylammonium-cations and their anions are varied, and in which the secondary components of the inorganic electrolyte solution are modified.

In Example 4, the application of the present example will be described.

EXAMPLE 4

In Example 1 it was explained, which the proportion between ammonium- and potassium-nitrate must be, in order to originate mixed crystals at an established temperature, the crystal form of which is isomorphous with the crystal form of the monoclinic ammonium nitrate III, which mixed crystals are able to adopt a lipophilic surface characteristic. A second condition for attaining this property is that the dissolved n-alkylammonium micells, at the aforementioned established temperature, are always sufficiently soluble and do not crystallize with destruction (or "dilution") of the lipophilic surface. To fulfill this condition, the necessary data are given in Example 3.

Combining the conclusion of Examples 1 and 3 it is possible to foresee, and even to "calculate," the "minimum temperature for maximum detonation ability" (MTMD).

Being, for instance, provided that a water containing explosive composition is needed with a MTMD of 15° C.; on combining Examples 1.2.4 and 3.3, the following composition is obtained: 15 parts of water; 66 parts of ammonium nitrate; 4.5 parts of potassium nitrate; 7.5 parts of sodium nitrate; 0.4 part of n-dodecylammonium-chloride; and 0.1 part of n-octylammonium-chloride. Here to a quantity of e.g., 5 parts of fuel oil Nr. 2 can be mixed for sensitizing, as well as e.g., 0.5 part of guar flour. (All figures are parts by weight.)

A second example consists in combining Examples 1.1.11 and 3.7 to obtain a water containing explosive with a MTMD of 0° C.; 15 parts of water; 66 parts of am-

13

monium nitrate, 9 parts of potassium nitrate, 0.2 parts of n-dodecylammonium-chloride, and 0.3 part of n-octylammonium-chloride. This mixture can, e.g., be used with 3.5 parts of fuel oil Nr. 2, 0.75 of polyacrylamide, and 20 of aluminum powder. (All figures are parts by weight.)

These "theoretical" explosive compositions were treated by means of practical trails, whereafter the following was verified:

(a) At the MTMD the maximum characteristics of the explosive are still conserved.

(b) The detonation of the explosives is also still possible at lower temperatures, generally at 5 to 10° C. below the MTMD which corresponds to the amine composition, because at these low temperatures the solubility of the n-alkylammonium micells gets very small, but does not reach a zero value.

(c) With reference to the MTMD which corresponds to the composition of the mixed crystals, the minimum temperature must be strictly observed.

If a water containing explosive is detonated at a temperature below its "theoretical" MTMD, a retrogression of its characteristics occurs rapidly, until its insensitivity is reached: Decrease of the critical density of the explosive; increase of the critical bore hole diameter; and increase of the critical booster weight. Such a retrogression occurs, for instance, when Examples 1.2.7 and 3.5 are combined, under the supposition that the MTMD would be 0° C.

Nevertheless, in presence of about 6 parts by weight of formamide, the MTMD subject to the amine composition may be lowered by 10 to 15° C., without provoking a substantial loss of the blasting performances.

EXAMPLE 5

A few methods of preparation of water containing blasting agents according to the invention will be described as follows:

Example 5.1

Into a heatable, insulated agitating container of a capacity of 1.200 liters, a quantity of 790 kgs. is pumped of a technically pure ammonium nitrate solution containing 14.9% of water and having a temperature of 85° C. Afterwards, 60 kg. of sodium nitrate and 65 kg. of potassium nitrate, both of synthetical quality, are dissolved. Into a separate container of a capacity of 20 liters, a quantity of 10 kg. of water is weighed, where to 3 kg. of hydrochloric acid at 36.5% is admixed. Subsequently, while agitating, 3.7 kg. n-dodecylamine and 1.3 kg. n-octylamine are added to this acid solution. The pH of the so obtained n-alkylammonium-chloride solution is regulated at a value of 5-5.5, adding small quantities of amines or acid, if necessary. This n-alkylammonium-chloride solution, together with 20 kg. of water, are admixed to the foregoing electrolyte solution. The so obtained total solution is introduced into a mixer provided with a cooling jacket. The jacket is fed with water of 20° C., and the solution is cooled so long until a temperature of 30° C. is reached. Meanwhile, a suspension comprising of 44 kg. of fuel oil Nr. 2 and 3 kg. of guar flour is prepared within a pressurized tank with a capacity of 75 liters. The suspension is mixed and maintained homogeneous by means of compressed air. This suspension is injected into the lower part of the cooler by means of compressed air and homogeneously mixed with the cooled pasty mass. A slurry is obtained, which is packed in polyethylene bags.

Example 5.2

Into the same heatable, insulated agitating container the following ingredients are mixed and heated up to 68° C.: 160 kg. of water; 670 kg. of ammonium nitrate (with a contents of 0.16% ammonium sulfate); 5 kg. of barium nitrate; 58 kg. of sodium nitrate (Chile salt-peter); and 50 kg. of synthetical potassium nitrate, obtaining a homogeneous solution. To this hot solution 2.5 kg. nitric acid at 63% are added; subsequently at separately prepared mixture consisting of 4.05 kg. of coco-amine and 0.65 kg. of technically pure n-octylamine is added. Mixing is carried

14

on until complete homogeneity; the pH is regulated as before at a value of 5.8-6. The total solution is continuously pumped through a thin layer heat exchanger, the cooling jacket of which is fed with water of 18° C. A quantity of 475.1 kg. of the cooled slurry is received at 22° C. in a mixer, whereafter the emerging slurry is branched out into a twin mixer. To the collected charge of 475.1 kg., 20 kg. of fuel oil Nr. 2 and a suspension consisting of 2.4 kg. of polyacrylamide and 2.5 kg. fuel oil Nr. 2 is homogeneously admixed. A water containing blasting agent is obtained, which can be packed in polyethylene bags or which can be filled into a tank-truck to be directly delivered into the bore holes of an open pit mine.

Example 5.3

Into the twin mixer of foregoing Example 5.2, a quantity of 402.5 kg. cooled slurry is collected. 80 kg. of a medium-fine aluminum powder of a purity of 99.8% and 12 kg. of fuel oil Nr. 2 are added, together with a suspension comprising 3 kg. of glycol and 2.5 kg. of self-complexing guar flour. After homogenizing, a slurry with extraordinary strength and brisance is obtained, which, e.g., is able to assure an extraordinarily favorable fragmentation of a hard and tough magnetite ore.

Example 5.4

In a heatable, insulated agitating container, a solution with 65° C. is prepared, comprising 170 kg. of water, 635 kg. of ammonium nitrate (with a contents of 0.10% ammonium sulfate), 3 kg. of barium perchlorate and 83 kg. of synthetic potassium nitrate. Separately, the n-alkylammonium salts are prepared as follows: (1) To a quantity of 40 kg. of formamide, 3.15 kg. of perchloric acid at 70% are admixed for the salifying with 4 kg. of n-dodecylamine. (2) In the same way, to 20 kg. of formamide 4.45 kg. of perchloric acid of 70% and, respectively, 4 kg. of n-octylamine are admixed. In both cases the pH is regulated at a value of 5-5.5. To the first-mentioned electrolyte solution the formamide-containing n-dodecylammonium-perchlorate solution is admixed, whereafter the total solution is continuously pumped through a thin layer heat exchanger, the cooling jacket of which is fed with water of 18° C. The rate of flow of the solution is controlled in such a way, that a cooled mother liquor-plus-crystals is obtained with a temperature of 30° C. This "paste" is collected in a mixer and homogeneously mixed with the formamide containing n-octylammonium perchlorate solution. Mixing is carried on with a suspension comprising 30 kg. of fuel oil Nr. 2 and 3.4 kg. of polyacrylamide. A water containing slurry results, which is especially suitable to be used at very low temperatures, below 0° C.

Example 5.5

In a heatable, insulated agitating container a solution with 60° C. is prepared, comprising 165 kg. of water, 650 kg. of ammonium nitrate, 40 kg. of sodium nitrate, 3.65 kg. of barium nitrate, 75 kg. of potassium nitrate, 4.35 kg. of hydrochloric acid at 36.5%, 4.5 kg. of n-dodecylamine, and 2.5 kg. of n-octylamine and 55 kg. of formamide. The pH is regulated at a value of 5.8-6.0. The solution is cooled down at 21° C. by means of a continuous thin layer heat exchanger. A quantity of 500 kg. of the cooled slurry is collected in a mixer, where to 60 kg. of medium-fine aluminum powder (99.9%), 5 kg. of milled carbon, 15 kg. of fuel oil Nr. 4, and 4 kg. of polyacrylamide are admixed.

Example 5.6

In a heatable, insulated agitating container a solution with 25° C. is prepared, comprising 75 kg. of water, 30 kg. of formamide, 145 kg. of ammonium nitrate, 2 kg. of barium nitrate, 20 kg. of potassium nitrate, 0.85 kg. of hydrochloric acid at 36.5%, 1 kg. of n-dodecylamine. This solution is pumped into a mixing device, whereafter 203 kg. of lipophilic mixed crystals are admixed which

were obtained (according to Example 7.1) with a humidity of 1.2% by weight. Finally a suspension is added which comprises 20 kg. of fuel oil Nr. 2 and 2.65 kg. of polyacrylamide, and mixing is carried on until complete homogeneity. By this method a slurry is obtained which is specially liquid and appropriated for application of the well-known mixing-and-loading system with a distribution truck in the vicinity of the bore holes of the mine.

EXAMPLE 6

According to the preparation methods of Example 5, several water containing explosive mixtures were prepared, which are detailed in the following tables. In all preparations a technical ammonium nitrate with a content of 0.12–0.15% of ammonium sulfate was used. The utilized sodium nitrate was in all cases Chile salt-peter, and potassium nitrate was of a synthetical quality. All the inorganic alkylammonium salts had been prepared previously according to the described methods, whereby the starting bases were commercially available alkylamines and acids. All the other secondary and additional components were of customary commercial quality. The applied swelling compounds correspond to the following types:

Guar flour (1): Trademark "MDC" of Messrs. "Stein Hall," New York.

Guar flour (2): Self-complexing guar flour "EXFC-50" of Messrs. "Stein-Hall," New York.

Polyacrylamide (3): Quality "Superfloc 84" of Messrs. "American Cynamid," New Jersey.

The employed aluminum powder was the 99.8% pure commercial quality "SA-22" of Messrs. "Alcan," Canada.

From Table 6.1 the influence of the selected alkylammonium salt on the blasting characteristics is made visible.

Table 6.2 illustrates how an increasing water contents is conducting towards a progressive detonation insensitivity.

Table 6.3 demonstrates in which way the presence of formamide improves the detonation sensitivity and simultaneously explains the influence of falling field temperatures.

Table 6.4 comprises an illustrative series of compositions according to the present invention.

Regarding these examples, it is to be observed that intentionally no use was made of self-explosives, for better illustration of the preferred compositions, although such a use would be absolutely possible, and whereby, however, the economical advantages of the preferred blasting agents are moved into the background.

To all the compositions of the four tables, 10–20% by weight of aluminum powder can be added, whereby

brisant-high explosives were created, and whereby the critical diameter of same is reduced about ½ to 1 inch (12.5–25 mm.).

The critical density of these compositions, i.e., their maximum density, which still allows a complete detonation of the charge, is found to lie between 1.15 and 1.55 and depends on the diameter of the charge, on the field temperatures and on the explosive composition.

The critical booster quantity, i.e. the minimum quantity of the priming explosive, which is necessary to guarantee a complete detonation, also depends upon these three conditions and varies between ½ and 1 lb. (38 and 450 gr.).

For comparison it should be reminded that the water bearing explosives according to U.S. Pat. No. 3,449,180 retain their complete capacity with falling temperatures only down to 20° C., whereafter a rapid insensitivity to detonation occurs.

TABLE 6.1

	Composition No.					
	6.1.1	6.1.2	6.1.3	6.1.4	6.1.5	6.1.6
Percent by weight:						
Water	15.00	15.00	15.00	15.00	15.00	15.00
Ammonium nitrate	66.00	66.00	66.00	66.00	57.00	47.00
Potassium nitrate	5.00	5.00	5.00	5.00	5.00	5.00
Sodium nitrate	7.50	8.00	8.00	7.90	7.90	7.90
Barium nitrate	0.50	0.50	0.50	0.50	0.50	0.50
Zinc nitrate, 6 aq.	0.80					
Nitric acid, 63%		0.28				
Hydrochloric acid, 36.5%			0.28			
Perchloric acid, 70%				0.40	0.40	0.40
n-Dodecylamine	0.45	0.45	0.45	0.45	0.45	0.45
n-Octylamine	0.05	0.05	0.05	0.05	0.05	0.05
Fuel oil No. 2	4.40	4.40	4.40	4.40	3.40	3.40
Guar flour (1)	0.30	0.32	0.32	0.30	0.30	0.30
Aluminium powder, 99.8%					10.00	20.00
Critical diameter, inches	4½	4	3½	2½	2½	2
Detonation velocity, m./sec. (for charges of 5 inches φ)	5,500	5,500	5,600	5,750	5,400	5,100
Air gap test:						
(a) For charges of 5 inches φ, inches	4	4	4	4	5	5
(b) For charges of 6½ inches φ, inches	6	6	6	6	8	12

TABLE 6.2

	Composition No.					
	6.2.1	6.2.2	6.2.3	6.2.4	6.2.5	6.2.6
Percent by weight:						
Water	12.00	14.00	16.00	18.00	20.00	22.00
Ammonium nitrate	70.00	68.00	66.00	64.00	62.00	60.00
Potassium nitrate	5.00	5.00	5.00	5.00	5.00	5.00
Sodium nitrate	7.00	7.00	7.00	7.00	7.00	7.00
Barium nitrate	0.50	0.50	0.50	0.50	0.50	0.50
Hydrochloric acid, 36.5%	0.28	0.28	0.28	0.28	0.28	0.28
n-Dodecylamine	0.45	0.45	0.45	0.45	0.45	0.45
n-Octylamine	0.05	0.05	0.05	0.05	0.05	0.05
Fuel oil No. 2	4.40	4.40	4.40	4.40	4.40	4.40
Guar flour (2)	0.32	0.32	0.32	0.32	0.32	0.32
Critical diameter, inches	3	3½	3½	3½	5	n.d.

NOTE.—n.d.=non-detonable.

TABLE 6.3

	Composition No.											
	6.3.1	6.3.2	6.3.3	6.3.4	6.3.5	6.3.6	6.3.7	6.3.8	6.3.9	6.3.10	6.3.11	6.3.12
Percent by weight:												
Water	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00	18.00
Ammonium nitrate	69.00	68.00	67.00	66.50	67.50	66.50	66.00	65.00	64.00	59.40	60.00	55.75
Potassium nitrate	7.00	7.00	7.00	7.00	9.00	9.00	9.00	9.00	15.00	15.00	15.00	15.00
Barium nitrate	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Formamide	4.00	5.00	6.00	7.00	3.00	4.00	5.00	6.00	7.00	5.90	4.80	5.90
n-Dodecylammonium perchlorate	0.60	0.60	0.60	0.60	0.60	0.60	.60	0.60	0.60	0.50	0.45	0.45
n-Octylammonium perchlorate	0.15	0.15	0.15	0.15	0.30	0.30	0.30	0.30	0.30	0.30	0.85	0.85
Fuel oil No. 2	3.00	3.00	3.00	2.50	3.50	3.50	3.00	3.00	3.00	2.90	2.90	2.90
Polyacrylamide (3)	0.75	0.75	0.75	0.75	0.60	0.60	0.60	0.60	0.60	0.50	0.50	0.65
Critical diameter at:												
20° C., inches	3	2	1½	3	3	2	1½	2	3			
10° C., inches	3	2	2	3	3	2	1½	2	3			
0° C., inches	n.d.	n.d.	n.d.	n.d.	4	3	2	2	3			
10° C., inches					n.d.	n.d.	n.d.	n.d.		3	3	3
18° C., inches										3	3	3

NOTE.—n.d.=non-detonable.

The preparations 6.3.1 to 6.3.9 were cooled down to 35° C. and then stored at progressively falling temperatures of 20, 10, 0, –10° C.

The preparations 6.3.10 to 6.3.12 were cooled down to 28° C. to be stored immediately at –10° C. and afterwards at –18° C.

All shots were made—after storage of 48 hours—the soonest possible at the established temperatures to avoid a gain of temperature of the samples.

TABLE 6.4

	Composition No.									
	6.4.1	6.4.2	6.4.3	6.4.4	6.4.5	6.4.6	6.4.7	6.4.8	6.4.9	6.4.10
Percent by weight:										
Water	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00
Ammonium nitrate	67.90	66.60	66.40	66.00	67.10	68.25	62.40	65.40	65.30	67.50
Potassium nitrate		5.00	9.00	5.00	7.00	7.00	6.00	5.00	9.00	7.00
Potassium chloride	5.00	3.00								
Sodium nitrate	7.00			7.00	2.00		6.00	7.00		
Calcium nitrate		5.00								
Barium nitrate	0.50	0.50	0.30	0.50	0.40	0.30	0.50	0.50	0.25	0.25
Urea							5.00	2.00		
Formamide					4.00					6.00
Acetamide						5.00				
Glycol			0.50				0.50		6.00	
Carbon				2.00						
Sugar			5.00							
Fuel oil No. 2	3.80	4.10	3.00	3.25	3.20	3.00	3.60	4.00	3.25	2.90
Coco-amine-perchlorate										0.60
Coco-amine-chloride	0.50		0.40	0.40						
n-Dodecylammonium chloride		0.40			0.50	0.60	0.40	0.40	0.50	
n-Decylammonium chloride		0.10		0.10			0.10	0.20		
n-Octylammonium chloride					0.10	0.15	0.10		0.20	
2-ethyl-hexylammonium chloride			0.10							
Guar flour (1)	0.30	0.30					0.40	0.50	0.50	
Guar flour (2)			0.30							
Polyacrylamide (3)				0.75	0.70	0.70				0.75
Critical diameter (at 10° C.), inches	5	4	4	3½	3	3	3	2	2	1½

EXAMPLE 7

Some preparation methods for the lipophilic mixed crystals applied for the pulverulent and water containing explosives according to the invention are described as follows:

Example 7.1

In an industrial vacuum evaporating device with a capacity of 1000 liters and equipped with a heating jacket and an agitator, solution is prepared comprising 100 liters of water, 510 kg. of ammonium nitrate plus 70 kg. of potassium nitrate and 3.7 kg. of zinc nitrate hexahydrate, which is warmed up to 85° C. In a separate container of 10 liters capacity, 1.5 kg. of coco-amine and 6 kg. of triethanolamine are homogeneously mixed. The amine-mixture is added to the foregoing electrolyte solution, as well as 10 g. of silicon oil as anti-foaming agent. Agitation is continued until complete homogeneity.

The heating jacket of the evaporator is regulated at 83–85° C. and a vacuum of 60–25 torr is maintained during 2.5 to 3.5 hours. The obtained lipophilic mixed crystals, which at the moment of discharge have a temperature of 55–65° C., are packed in bags.

Example 7.2

In the same vacuum evaporating device, a solution is now prepared comprises 100 kg. of water, 570 kg. of ammonium nitrate, 30 kg. of potassium nitrate, 2 kg. of coco-amine-acetate and 10 g. of silicon oil. The evaporation of the water takes place under the same conditions as in case of Example 7.1.

Example 7.3

In a container of 10 liters capacity, 0.7 kg. of hydrochloric acid at 36.5% is admixed to 5 liters of water, whereafter 1.3 kg. of molten n-dodecylamine is added. This mixture is homogenized and, if necessary, smaller quantities of acid or amine are added for the purpose to obtain a final pH value of 5 to 5.5. During this salification of the amines, the temperature rises only up to approximately 45° C., wherefore a forced cooling is not necessary.

Separately, a solution that comprises 90 liters of water, 560 kg. of ammonium nitrate and 65 kg. of potassium nitrate is prepared in the vacuum evaporator; the n-dodecylammonium chloride solution and 10 g. of silicon oil are homogeneously admixed to the hot solution. The evaporation of the water takes place under the same condition as in case of method 7.1.

Further variations

In other preparations, according to methods 7.1, 7.2 and 7.3, modifications of composition are introduced,

wherein the percentages by weight of potassium nitrate, n-alkylamine salt and triethanolamine, as well as the nature of the amine salts and the humidity of the final product are varied. All these preparations are reserved for the production of the different explosive mixtures of Example 8.

EXAMPLE 8

According to the method described in Example 7.1 several charges of lipophilic mixed crystals were prepared in changing compositions and contents of humidity. After resting time of 24 hours, 94.5 parts of weight of lipophilic mixed crystals were blended with 5.5 parts by weight of fuel oil Nr. 4. Different explosives of the below indicated composition were obtained. The explosives were filled into cartridges of 22.0 mm. and 28.0 mm. diameter and stored during 3 months at a room temperature which fluctuated from 13 to 19° C., whereafter the explosion characteristics are determined. (All shots were set off by means of an aluminum blasting cap Nr. 6 of brand "Briska.")

Examples 8.1.1 and 8.1.2 are intended to recall the prior art: Example 8.1.1 is simply based on an adsorption of n-alkylamine on pure ammonium nitrate which, as already known, is unable to produce cap-sensitive ammonium nitrate-fuel oil explosives at room temperature: Example 8.1.2 corresponds to the status of Pat. No. 3,449,180. Examples 8.1.3 to 8.1.6 describe compositions according to the present invention, which are based on lipophilic mixed crystals, in absence of secondary auxiliary substances. Examples 8.1.7 to 8.1.11 correspond to other compositions according to the invention, wherein the addition of an auxiliary substance enhances the sensitivity of the explosive mixtures. In all these examples, and for reason of comparison, only one triethanolammonium salt was chosen. In Example 8.1.12 an inorganic n-alkylammonium salt was applied, whereby, as noticeable, less sensitive ammonium nitrate-fuel oil explosives can be obtained (being in this case the pH of the aqueous medium of a considerably lower value, a fact which shifts the affinity of the micells towards this aqueous phase).

Furthermore, it is observed that the presence of potassium nitrate does not cause a substantial loss of strength, but that it results in an interesting increase of brisance. A rising percentage of humidity causes a gradual decay of the blasting characteristics. In these pulverulent explosives, and subject to the kind of composition, a water contents of up to about 3% represents a limit which should not be exceeded, in order to assure a detonation sensitivity to a common blasting cap.

In the following Tables 8.2 and 8.3 other compositions according to the invention are shown, which have been prepared as formerly described. In all these cases, the alkylamines were salified in situ by organic acids or by

TABLE 8.1

	Composition No.											
	8.1.1	8.1.2	8.1.3	8.1.4	8.1.5	8.1.6	8.1.7	8.1.8	8.1.9	8.1.10	8.1.11	8.1.12
Percent by weight:												
Water	0.35	0.40	0.10	0.40	0.45	3.55	0.90	0.75	3.40	4.50	0.50	0.20
Ammonium nitrate	93.25	93.10	88.75	83.70	88.00	85.10	89.25	87.00	84.60	84.00	85.00	84.00
Potassium nitrate			4.75	9.50	4.75	4.60	2.35	4.75	4.55	4.25	7.00	9.50
Barium nitrate	0.50	0.50	0.50	0.50	0.50	0.48	0.50	0.50	0.45	0.45	0.50	0.50
Zinc nitrate (6 aq.)	0.15	0.50	0.15	0.15	0.30	0.29	0.50	0.50	0.50	0.50	0.50	0.50
Coco-amine	0.25	0.25	0.25	0.25	0.50	0.48	0.25	0.25	0.25	0.25	0.25	0.25
Triethanolamine		0.75					0.75	0.75	0.75	0.75	0.75	0.75
Dodecylammonium chloride												0.30
Fuel oil No. 4	5.50	5.50	5.50	5.50	5.50	5.50	5.50	5.50	5.50	5.50	5.50	5.50
Explosion characteristics:												
Weight strength according to Trauzl (net cm. ³)	00	375	380	370	380	350	375	375	365	350	380	360
Brisance according to Hess (with steel plate of double thickness) mm	00	15.5	18.1	16.2	19.7	14.5	18.3	19.0	15.8	00	18.2	13.0
Detonation velocity according to Dautriche (zinc pipe 30 mm. φ) m./sec.	00	3,950	4,180	3,740	4,360	2,630	4,060	3,880	3,480	00	4,080	2,840
Air gap test on sand, in φ 22 mm. per length of 175 mm.-cm.	0--	2	2	2	2	0-	2	4	6	0--	2	0
Air gap test on sand, in φ 28 mm. per length of 175 mm.-cm.	0--	4	4	4	4	0-	6	8	8	0--	6	0

Symbols: 00, insensitive to blasting cap No. 6; 0, transmission of detonation when cartridge tips touch each other (gap=0); 0-, no transmission of detonation in case of touching cartridges (the primed cartridge explodes completely); 0--, no transmission of detonation in case of touching cartridges (the primed cartridge does not go off).

an inorganic acid salt. The use of inorganic free acids was intentionally avoided. Table 8.3 illustrates some compositions, in the case of which a considerable increase of strength and brisance is obtained through addition of aluminium powder. In these compositions the aluminium was added to the lipophilic mixed crystals together with the fuel oil.

Attention is called to the fact that for all the compositions of Tables 8.1, 8.2 and 8.3 use was made of a technical ammonium nitrate which contained about 0.2% by weight of ammonium sulfate, due to which reason in all the preparations of mixed crystals a certain quantity of a barium salt was added.

All the blasting characteristics shown in Tables 8.2 and 8.3 were determined first after storing the cartridges during 3 months at a temperature of 13 to 19° C.

TABLE 8.2

	Composition No.					
	8.2.1	8.2.2	8.2.3	8.2.4	8.2.5	8.2.6
Percent by weight:						
Water (humidity)	0.20	0.30	0.20	0.40	0.25	0.50
Ammonium nitrate	88.50	89.30	89.80	84.90	84.05	86.20
Potassium nitrate	4.00	5.00	5.00	7.00	8.00	8.00
Barium nitrate	0.30		0.30	0.30		0.30
Barium perchlorate		0.30			0.30	
Coco-amine	0.20		0.50	0.30	0.20	0.20
n-Dodecylamine	0.10	0.30		0.10	0.20	0.20
n-Decylamine			0.10	0.10		0.10
n-Octylamine	0.05	0.10			0.10	0.10
Triethanolamine	1.00			1.20	1.30	
Formic acid (100%)	0.45	0.11				
Acetic acid (100%)			0.19	0.64		
Lactic acid (100%)					1.04	0.31
Fuel oil No. 2	5.20		3.91		4.58	
Fuel oil No. 4		4.59		5.06		4.09
Explosion characteristics:						
Weight strength according to Trauzl (net cm. ³)	375	365	370	365	380	375
Brisance according to Hess (with steel plate of double thickness) mm	19.5	17.7	17.1	18.7	19.0	17.0
Detonation velocity according to Dautriche (zinc pipe 30 mm. φ) m./sec.	4,260	4,060	3,980	4,300	4,100	3,910
Air gap test on sand, in 22 mm. φ per length of 175 mm.-cm.	4	2	2	4	4	2
Air gap test on sand, in 28 mm. φ per length of 175 mm.-cm.	6	4	4	6	6	4

TABLE 8.3

	Composition No.					
	8.3.1	8.3.2	8.3.3	8.3.4	8.3.5	8.3.6
Percent by weight:						
Water (humidity)	0.50	0.60	0.40	0.45	0.55	0.35
Ammonium nitrate	80.45	78.25	80.50	75.50	73.30	75.55
Potassium nitrate	5.00	5.00	5.00	5.00	5.00	5.05
Barium nitrate	0.50	0.50	0.50	0.50	0.50	0.50
Zinc nitrate (6 aq.)	0.20	0.90		0.20	0.90	
Triethanolamine		1.40			1.40	
Coco-amine	0.35	0.35		0.35	0.35	
Coco-amine-acetate			0.60			0.60
Fuel oil No. 4	3.00	3.00	3.00	3.00	3.00	3.00
Aluminum powder	10.00	10.00	10.00	15.00	15.00	15.00
Explosion characteristics:						
Weight-strength according to Trauzel (net to cm. ³)	470	490	475	480	510	490
Brisance according to Hess (with steel plate of double thickness) mm	19.2	20.5	19.0	20.2	22.1	19.8
Detonation velocity according to Dautriche (zinc pipe 30 mm. φ) m./sec.	4,200	4,360	4,150	3,650	3,950	3,720
Air gap test on sand, in 22 mm. φ per length of 175 mm.-cm.	4	4	4	6	6	6
Air gap test on sand, in 28 mm. φ per length of 175 mm.-cm.	6	6	6	8	8	8

While I have disclosed several embodiments of the present invention, it is to be understood that these embodiments are given by example only and not in a limiting sense.

I claim:

1. A pulverulent or water bearing explosive mixture, comprising
 - 0 to 20% by weight of water,
 - 3 to 6% by weight of liquid hydrocarbons,
 - 50 to 97% by weight of mixed crystals produced by co-crystallization of ammonium nitrate and potassium salts,
- said mixed crystals having a crystal form that is isomorphous with the monoclinic crystal form of ammonium nitrate III,
- said mixed crystals having a lower temperature of crystal form transition than 32.2° C., which is the normal lower temperature of transition of pure ammonium nitrate III,
- said mixed crystals being crystallized between 100 and 20° C., in the presence of salts of primary amino alkanes having chain lengths ranging from C₃ to C₁₈, and

- said mixed crystals having a lipophilic surface characteristic, stable at temperatures below 32.2° C.
2. The mixture, as set forth in claim 1, wherein said ratio by weight of ammonium nitrate and potassium salts is from 20/1 to 4/1.
3. The mixture, as set forth in claim 1, wherein said salts of primary amino alkanes are in the amount of 0.2 to 1.5% by weight.
4. The mixture, as set forth in claim 1, wherein said mixed crystals have a lipophilic surface characteristic, stable at temperatures between -20 and +20° C.
5. The mixture, as set forth in claim 1, wherein said potassium salt is potassium nitrate.
6. The water bearing explosive mixture, as set forth in claim 1, further comprising an amount of such salts and substances, which are able to depress the saturation temperature of a total hot starting solution down to 60° C., at constant water contents, said depression of saturation temperature decreasing of the solubility of co-dissolved alkylammonium micells, and said decrease of the solubility of said co-dissolved alkylammonium micells increasing the adsorption stability of same on the surface of the mixed crystals, at upper temperatures.
7. The water bearing explosive mixture, as set forth in claim 6, wherein said amount of said salts and substances are from 4 to 8% by weight.
8. The water bearing explosive mixture, as set forth in claim 6, wherein said salts and substances are sodium nitrate.
9. The water bearing explosive mixture, as set forth in claim 6, wherein said salts and substances are calcium nitrate.
10. The water bearing explosive mixture, as set forth in claim 6, wherein said salts and substances are sodium- and calcium nitrate.
11. The water bearing explosive mixture, as set forth in claim 1, further comprising an amount of such substance which is able to increase the solubility of co-dissolved alkylammonium micells at temperatures below 20° C., and said increase of solubility of the co-dissolved alkylammonium micells enhancing the adsorption stability of same on the surface of the mixed crystals, at the lower temperatures.
12. The water bearing explosive mixture, as set forth in claim 11, wherein said amount of said substance is from 5 to 7% by weight.
13. The water bearing explosive mixture, as set forth in claim 11, wherein said substance is formamide.
14. The pulverulent explosive mixture, as set forth in claim 1, wherein said lipophilic mixed crystals are crystallized in the presence of an amount of such substance, which is able to increase the solubility of co-dissolved alkylammonium micells in the low water bearing solution, which wets the dried mixed crystals, at a temperature below 20° C., and said increase of the solubility of the co-dissolved alkylammonium micells enhances the adsorption stability of same on the surface of said mixed crystals, at lower temperatures.
15. The pulverulent explosive mixture, as set forth in claim 13, wherein said amount of said substance is from 1 to 2% by weight.
16. The pulverulent explosive mixture, as set forth in claim 13, wherein said substance is an alkanolammonium salt with 2 or 3 carbon atoms in each alkyl chain.

17. The pulverulent or a water bearing explosive mixture, as set forth in claim 1, further comprising a metallic powder.
18. The pulverulent or a water bearing explosive mixture, as set forth in claim 17, wherein said metallic powder is in the amount of from 0 to 20% by weight.
19. The pulverulent or a water bearing explosive mixture, as set forth in claim 17, wherein said metallic powder is aluminum powder.
20. A process of producing a pulverulent or water bearing explosive mixture with 0 to 20% by weight of water, and an amount of lipophilic mixed crystals which is crystallized out of saturated starting solutions between 100 and 20° C., in the presence of salts of primary amino alkanes having chain lengths ranging from C₈ to C₁₈ preferably in an amount of 0.2 to 1.5% by weight, and which is sensitized by liquid hydrocarbons in a preferred amount of 3 to 6% by weight, comprising the step of containing in the saturated starting solution potassium salts which are easily soluble in water, as components of the finished explosive, in order to maintain the lipophilic surface characteristic at lower temperatures, as for instance, 32.2° C., in particular between -20 and +20° C., which has the characteristic of forming with ammonium nitrate, mixed crystals, the crystal form of which is isomorphous with the crystal form of ammonium nitrate III, said mixed crystals having a lower temperature of crystal form transition than 32.2° C., which is the normal lower temperature of transition of pure ammonium nitrate III.
21. The process, as set forth in claim 20, wherein said potassium salts are potassium nitrate.
22. The process, as set forth in claim 20, wherein said potassium salts are in the amount of 3 to 15% by weight.
23. The process of producing a water bearing explosive mixture, as set forth in claim 20, further comprising the step of adding to the saturated hot starting electrolyte solutions such salts or substances which decrease the saturation temperatures of said electrolyte solutions at a constant water content for decreasing the solubility of alkylammonium micells at higher temperatures than 60° C. and for stabilizing micells adsorbed on said mixed crystals.
24. The process, as set forth in claim 23, wherein said salts or substances are sodium nitrate.
25. The process, as set forth in claim 23, wherein said salts or substances are calcium nitrate.
26. The process, as set forth in claim 23, wherein said salts or substances are sodium nitrate and calcium nitrate.
27. The process, as set forth in claim 23, wherein said salts or substances are in a quantity of 4-8% by weight.
28. The process of producing a water bearing explosive mixture, as set forth in claim 20, further comprising adding to the explosive mixture such substances which increase the solubility of the alkylammonium micells at lower temperatures than 20° C. and for stabilizing the micells adsorbed on the mixed crystals.
29. The process, as set forth in claim 28, wherein said substances are formamide.
30. The process, as set forth in claim 28, wherein said substances are in the amount of 5 to 7% by weight.
31. The process of producing a pulverulent explosive mixture, as set forth in claim 20, wherein adding to the hot starting solutions for crystallizing the mixed crystals substances which increase the solubility of alkylammonium micells at lower temperatures than 20° C. and for stabilizing the micells adsorbed on the mixed crystals and which are able to

23

provoke the increase of the solubility of the alkyl-ammonium micells in a water poor final product.

32. The process, as set forth in claim 30, wherein said substances are alkanol ammonium salts easily soluble in water, having an alkyl chain length ranging from C₂ to C₃. 5

33. The process, as set forth in claim 30, wherein said substances are in an amount of 1 to 2% by weight.

34. The process, as set forth in claim 20, further comprising using metallic aluminum powder. 10

35. The process as set forth in claim 34, wherein

24

said aluminum powder is used in the amount of 0 to 20% by weight.

References Cited

UNITED STATES PATENTS

3,449,180 6/1969 Vercauteren ----- 149—46 X

CARL D. QUARFORTH, Primary Examiner

S. J. LECHERT, JR., Assistant Examiner

U.S. Cl. X.R.

149—7, 40, 44, 46, 61