

March 18, 1952

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2,589,532

NITRATE EXPLOSIVE CONTAINING ALUMINUM

Filed June 11, 1948

2 SHEETS—SHEET 1

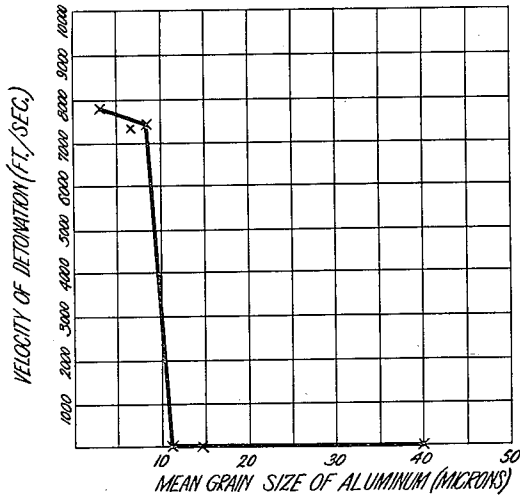


Fig. 1.

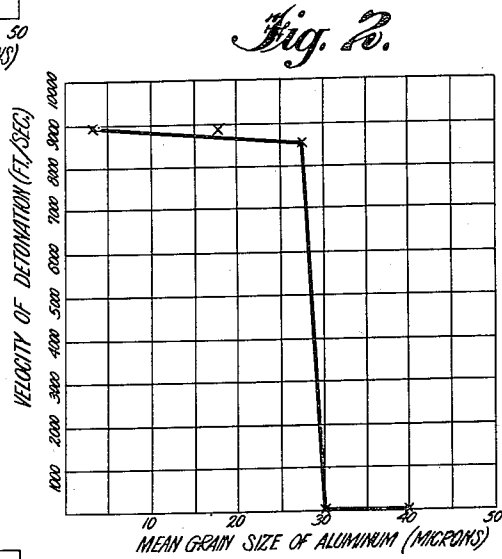


Fig. 2.

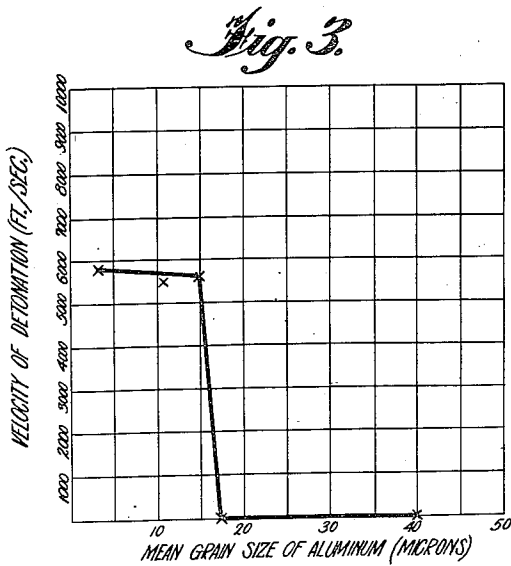


Fig. 3.

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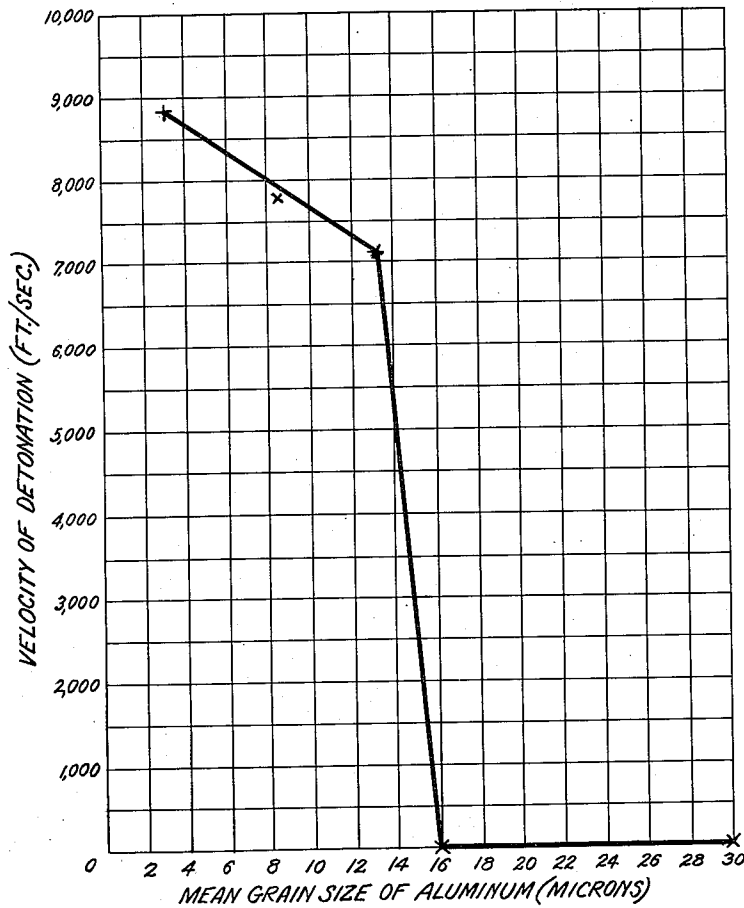
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2 SHEETS—SHEET 2

Fig. 4.



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UNITED STATES PATENT OFFICE

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NITRATE EXPLOSIVE CONTAINING
ALUMINUMLaud S. Byers, Reno, Nev.; Anna Rosalie Nelson
Byers executrix of said Laud S. Byers, deceased

Application June 11, 1948, Serial No. 32,496

2 Claims. (Cl. 52-15)

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This invention relates to explosive compositions and more particularly but not exclusively to alkali nitrate compositions in which ammonium nitrate is the predominating explosive ingredient.

The main object of the invention is to increase the power, sensitiveness and brisance of an ammonium nitrate explosive composition not only by controlling the grain size of the nitrate, but more especially by adding thereto a metallic activator in the form of atomized easily oxidizable atmospherically stable metal having a minute critical grain size.

Another object of the invention is to make use of the atomized metal in the form of granules or nodules, as distinguished from flakes, so as to reduce the tendency of the particles to become suspended in the air during manufacture of explosives containing the same.

The objects stated above contribute to both the safety and economy of manufacture and use of explosives, and make it possible, in an unexpected manner, to utilize alkali nitrate explosives under conditions and for purposes which hitherto required the use of materials having inherently greater velocities, requiring much greater care in manufacture and use, and thus more costly.

Additional objects and advantages will be apparent from the following description when it is read in conjunction with the accompanying drawings in which Figure 1 is a graph in which a typical explosive composition embodying the invention, designated Example 1 herein, has its velocity of detonation plotted as a function of the mean grain size in microns of atomized aluminum used in the composition.

Fig. 2 is a similar graph of the composition designated Example 2.

Fig. 3 is a graph of the composition designated Example 3, and

Fig. 4 is a graph of the composition designated Example 4.

This invention is predicated upon the fact that the effect of metallic activators of lower micron sizes in explosives, especially explosives of the ammonium nitrate type, improves as the ingredients are more intimately combined in what might be characterized substantially molecular contact. In the prior art, the effecting of such contact was dependent largely upon a compacting operation, and the particle size of the metallic activator had a direct effect upon the closeness of this contact.

The discovery of improved methods of making

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powdered metals such as aluminum wherein the molten metal is atomized and the finest grains are separated by an airfloat process has made available for the first time an atomized metal having a grain size down to one micron or less, permitting closeness of contact never before achieved. On a quantity production basis all of the particles will have a sub-sieve grain size and a diameter of 30 microns or less. Until very recent times, metal powder having a fineness below a Tyler 200 mesh (74 microns) was practically unknown.

This improved product, speaking particularly of aluminum, can be produced either as "flake powder" or "grained powder," the former, as its name implies, being in thin flat flake form and the latter in the form of spheres, or sausage-shaped or nodular granules. Flake aluminum, which is produced by grinding a coarse powder in a ball mill or by other methods has a tendency to float in the air due to its low apparent density. Since it is easily ignited in the presence of air there is an attendant danger of violent explosion upon ignition. Consequently, this flake type of powder is highly dangerous to use in the manufacture of explosives, as its tendency to float in the air, either unconfined in a mixing room or confined in a mixer, constitutes an ever-present hazard almost forbidding its use for such purposes.

The granular atomized metal presents none of these difficulties even when reduced to a size of 1 micron or less. The irregular granules are relatively hard to ignite, but when mixed with oxygen-releasing materials they will burn with heat and light evolution. Their high apparent density and low surface area tend to prevent them from becoming suspended in the air, so that danger of explosion or fire from aluminum fog is almost nil.

The present invention involves the discovery that when an atomized metal in the lower micron sizes is used in explosives, and more particularly in nitrate explosives, either with the metal particles as nuclei for the nitrate crystals, or as an exterior coating for the same, or are otherwise admixed with the nitrate there results an explosive which may be detonated by an ordinary #6 commercial blasting cap and one which shows good propagation characteristics. Previously available coarser metal powders due to their poor covering power cannot be used to produce a commercial explosive since an explosive using a coarser metal powder as a sensitizer cannot be detonated by a commercial blasting cap even if the

coarser metal powder is used in a much larger quantity than the atomized metal in the lower micron size range. This is particularly true in the case of materials such as ammonium nitrate which, in the parlance of the art, are not "cap-sensitive," that is, they require the addition of a sensitizer. Furthermore the micron size at which detonation occurs is critical as will be pointed out hereinafter. The invention will be described in both its applications, and examples of satisfactory proportioning of ingredients given.

Producing intimate contact between nitrate crystals and metal particles is difficult, but I have found that by the use of nitrate solutions of controlled saturation the metal particles may be made to seed the solution and produce crystals of the nitrate each having a metal particle as a nucleus. Such a result was practically impossible to attain with the large and heavy metal particles of the prior art, and when attempted required excessive amounts of metal. The new process, furthermore, insures uniform quality of product and freedom from separation during shipment, storage and handling.

The invention will first be described as directed to the production of a product in which the metal particles form nuclei for the nitrate crystals.

The activating agent, reduced to a grain size in which all particles are 30 microns, or less, in size is distributed throughout a solution from which the explosive oxidizing agent is crystallized, and means provided to prevent separation during crystallizing, to obtain a product in which the individual particles consist of crystals built around completely embedded particles of the activating agent. This building up of the explosive nuclei may and probably does occur in two ways.

It is a well established fact that due to the growth of crystals, even in a super-saturated solution, it is frequently necessary to "seed" the solution. This is effected either by adding minute crystals of the solution itself or minute solid foreign particles such as dust. Therefore when the crystals start to form in the present process some of the minute particles of the activating agent serve as the "seeds" which initiate the crystal growth and serve as nuclei around which the crystals continue to grow.

After the crystal growth has once started, it is probable that a second well-known physical phenomenon takes place, namely that other particles of the activating agent become bound to them by an intense force of adhesion. It is probable that this is due to di-pole attraction between the molecules of the nitrate and those of the activating agent. In all cases of anisotropic crystals this adhesive force is greater on the particle face which results in distorting the continued growth of crystals.

Theoretically it should be advantageous to have just as many particles of activating agent present as there are crystals formed, and the actual percentage of such agent by weight will, therefore, be a function of the size of the crystal particles. It is apparent that the maximum quantity of aluminum particles which will combine with the nitrate crystal either in the form of seeds or as embedded matter adhering to the partially developed crystal faces, should be used. When less than this amount is used, it is impossible to separate them mechanically, whereas, if a greater amount is present they can be easily rubbed or shaken out of the finished composi-

tion when dry. Though slight excess may serve to increase the temperature of explosion and consequently the volume of the gases, tests have proven that such excess does not affect either the sensitivity (gap test) or brisance.

Generally stated, the method of embedding the minute metal particles within the nitrate crystals or particles is to mix the required metal powders in an aqueous solution of the nitrate or nitrates, and then crystallize out the nitrate or compound nitrate salts while stirring or otherwise thoroughly mixing the mass to prevent separating out of the metal powder and insuring its entrapment within and throughout the nitrate crystals and particles. The mass is then dried, grained to the desired coarseness depending on its proposed use, and finally the grains are impregnated or coated with a fluid or melted nitro body as a moderant, preferably D. N. T. oily, to form the finished product. The amount of this moderant may be from about 5% to 15% of the weight of the mass to be coated.

However, to avoid the necessity of driving out most of the water from the aqueous solution of the nitrate by heat and vacuum or air currents in order to crystallize out the salt, I prefer to employ a super-saturated "mother liquor" kept liquid by sufficient applied heat as from controlled steam coils. The amount of supersaturation is kept equal to the amount of nitrate wanted for the batch being made, so that if the temperature of the supersaturated liquor is lowered to room temperature—say 20° C.—just this excess amount of nitrate will be crystallized out in the liquor and may be strained or centrifuged out, and another batch made by again adding the same excessive amount of nitrate salt to the mother liquor and again raising its temperature until all is dissolved, and then proceeding as before.

The atomized metal powder is preferably introduced after all the nitrate is dissolved, and the mass is kept thoroughly stirred or mixed during the cooling and crystallizing step. By this means the metal particles will become incorporated or embedded within the body of the individual nitrate crystals, although if an excess of metal powder is used there will also be a coating of the powder in closely adherent relation to the outer surface of the nitrate particles.

By the above method no evaporation of the "mother liquor" is required, but what little water is taken away with the wet crystals above its water of crystallization should, of course, be made up each time by the addition of an equal quantity of mother liquor of equal density at 20° C. with the mother liquor in the container.

As what constitutes "supersaturation" of such a salt of the alkali nitrates depends on the precise temperature of the liquid, it follows that if a large volume of mother liquor be used, relative to the batch amount of crystals wanted, it will only be necessary to raise and lower the temperature of the mass a few degrees to secure the desired amount, whereas with less mother liquor to start with (saturated at say 20° C.) it will be necessary to elevate the temperature considerably higher to insure solution of the added batch amount. Hence the larger amount of mother liquor permits operating at a much lower temperature.

The exact details of the procedure will depend somewhat upon the particular type of equip-

ment used but an example of the process is approximately as follows:

1000 pounds of mother liquor (saturated solution of ammonium nitrate at room temperature—say 20° C.) are run into the crystallizing tank and the stirrer started. The heat is then turned on in the steam coils or steam jacket and 1000 pounds of solid or dry ammonium nitrate added. This solid ammonium nitrate may contain a moderate moisture content, which is equalized out in the drying of the new crystals formed. Heating and stirring is then continued until all the nitrate is in solution.

The atomized metal is then stirred into the hot solution and when this is completely suspended throughout the solution the heat is turned off and cooling started. Vigorous stirring is necessary to keep the activating material evenly distributed throughout the solution. The time of cooling depends on the size of nitrate crystals desired, the faster the cooling the smaller the crystals.

When the temperature of the batch has been reduced to 20° C. again, the batch is discharged into a centrifugal machine for removal of the mother liquor in which the crystals are suspended. The separated mother liquor is run to a storage tank for use in a following batch and the crystals are removed from the centrifuge and dried.

The dried crystals are then placed in a suitable mixer where they are coated with the moderant or nitro-body. If D. N. T. oily is used it will require about 100 pounds for the above size batch.

Although the foregoing process relates only to the use of ammonium nitrate as an example, other nitrates separately and in combination can be used in this process to produce different types and different grades of explosives. The use of the atomized metal is also advantageous where explosive ingredients other than alkali nitrates are used. Of course, where only a small quantity of water is used to dissolve the nitrate or mixed nitrates with appropriate heat, and this water is driven off followed by cooling to effect the crystallization, only the exact amount of powdered activator need be introduced in the container as it will all be incorporated within the nitrate crystals, and no attention need be paid to differences in solubility or crystallizing temperatures when mixed nitrates are used.

My process as above described will be seen to make use of the known fact that if minute particles of any solid or "foreign" material are suspended in a solution from which crystals of a dissolved material are formed, the crystals have a tendency to build up around the solid particles, and this fact is taken advantage of in my process to obtain a most intimate mixture of ammonium nitrate and sensitizing material by actually building up the crystals on and around particles of the atomized metal suspended in the hot solution.

The proportionate ranges of the principal preferred ingredients which I have found useful for various explosive effects to meet most industrial requirements are approximately as indicated in the following example.

EXAMPLE A

	Parts by weight
Ammonium nitrate -----	80 to 90
Sodium nitrate -----	3 to 8
Atomized aluminum powder -----	0.5 to 1.5
Dinitrotoluene coating -----	5 to 15

Other similar nitro bodies or moderants as herein mentioned may be used. Also, as stated, other metals may be used; also, various moderants may be incorporated to secure special results as known in the art.

The explosive may be made with ammonium nitrate as the only nitrate salt, or with a percentage of either sodium or potassium nitrate or both of them as modifying agents, and finally the dried product is grained and preferably coated or impregnated with a film of D. N. T. oily to form the completed explosive. Other well-known explosive modifying agents may also be incorporated, and other explosive nitric esters may be used as the coating agent, such as any of the nitrotoluenes, nitrobenzenes, nitronaphthalenes, as well as nitroglycerine and nitroglycol, but the dinitrotoluenes give a protective coating to the granules against the hygroscopic tendency of the ammonium nitrate. Besides aluminum I have used magnesium and zinc in atomized form singly and in various admixtures, but I prefer the atomized aluminum powder as it has proven to be safer than magnesium, and better than zinc, for instance. Also I prefer as a nitrate salt, a compound crystallization of ammonium and sodium nitrates made from mixed solutions of these salts in proportion of, but not limited to, 5% of sodium nitrate to 95% of ammonium nitrate, as a small quantity of the sodium salt is a definite aid in the decomposition of the ammonium nitrate.

The improvement in the present explosive over prior art uses of carbon as an activator is marked. The explosive reaction is more complete due to the metal producing a quicker, higher temperature, and explosives containing it will fire under conditions where firing would otherwise be impossible. In using a metal as the fuel for the oxygen of the oxidant there seems to be a progressive rise in temperature from one explosive nucleus to the next and this serves to activate the entire mass and carry the explosive wave throughout the explosive charge. This is proved by the fact that with a given ammonium nitrate composition, and with the reaction activated by atomized aluminum, it will jump six inches from cartridge to cartridge in the "explosion-by-influence" test rather than two inches (referring to a standard dynamite paper cartridge, 1¼ x 8"), when activated by finely divided charcoal. This goes to prove that not only is there a more rapid decomposition of the ammonium nitrate crystal, but a more complete combustion as well.

In a mechanical mix of ingredients such as ammonium nitrate and activating agent there are inevitably areas in which there will be several contiguous particles of the nitrate coupled together and other areas in which there will be little groups of the activating agent, as well as numerous places where the surfaces of the particles do not fit together or touch one another, and it becomes necessary to add additional activating or sensitizing agents to permit the mixture to detonate. The explosive wave and high temperature effectively produced at the point of contact between the explosive component and the activating agent cannot be sustained at uniform rate if it has to travel through intermediate air spaces and intervening groups of the explosive component particles which are all of one kind not having immediate particles of the activating agent contiguous to or in contact with them. This explains why in such mechanical mixtures it is necessary to employ much greater proportions of the acti-

vating agent than in the same proportions of the same materials made up in accordance with the foregoing process, to secure comparative explosive efficiency.

A typical example of such a mechanical mixture wherein atomized, easily oxidizable metal in the form of aluminum is employed as an exterior coating is the following:

EXAMPLE B

	Per cent by weight
Ammonium nitrate-----	88
Atomized aluminum powder (-25 micron)---	4
Wood pulp-----	2
Nitro-body (nitrotoluene derivatives preferred)-----	6

In the above composition, it is preferred that the ammonium nitrate form the core or nucleus of the explosive units in the form of pellets, and that it be coated with the other ingredients of which the nitro-body serves in the nature of a binder.

In forming explosive pellets of the above composition the ammonium nitrate is pelleted or grained to a size depending upon the rate of decomposition desired.

This pelleted nitrate is placed in a suitable tumbler or mixing bowl; the atomized aluminum powder and wood pulp added, and while under rotation the liquid nitro body is added to the revolving and rolling mass, preferably in the form of a fine spray to form a slightly sticky film of the nitro-body about each pellet of the nitrate, and the mixing continued until a homogeneous mass is obtained.

The coating of the nitrate pellets or grains as described should be carried out at a temperature sufficiently above the setting point of the particular liquifiable nitro-body being used, so that this binding agent will remain in fluid condition until the completion of the coating operation.

Instead of the nitrotoluenes, nitroglycerine, nitroglycol, the nitrobenzenes or nitronaphthalenes may be used. It may be advantageous in certain compositions where a high gap test by the "explosion by influence" method is desired to use nitroglycerine or nitroglycerine-nitroglycol mixtures to replace all or part of the other nitric esters used.

I have found that the rate of decomposition of the ammonium nitrate grain varies with the size of the grain. As an example, in the explosive combination just referred to, if the nitrate grain has a mesh size all passing a 20 mesh screen and substantially all retained on a 60 mesh screen, the velocity of the explosive will be approximately 8,000 feet per second. If all the grains pass through a 60 mesh screen and substantially all are retained on a 100 mesh screen, the velocity of the explosive will be approximately 10,000 feet per second; whereas, if all the grains pass a 100 mesh screen and substantially all are retained on a 200 mesh screen, the velocity of the explosive approximates 12,000 feet per second, and so on. This variance in velocity or rate of detonation is accomplished by changing the grain size of the nitrates only, and not by changing the formula or the respective percentage by weight of any of the ingredients in any wise.

While the total volume of the expansive gases generated is the same in each instance, the rate at which these gases are liberated differs in each instance; that is, the smaller the size of the grain the quicker the generation and release of the gases.

In the explosive combination above referred to, tests in the ballistic mortar have shown a relative strength of 131 as against 100 T. N. T., and 132 as against 100 for T. N. T., in the Trauzl test for relative expansion of gases

While the explosive successfully passes the anvil-friction test with both the steel shoe and fiber shoe, it can still be completely detonated with a No. 6 commercial blasting cap.

As indicated above, the rate of decomposition of the ammonium nitrate grain varies with the size of the grain and the velocity of an ammonium nitrate explosive composition may be increased by as much as 4,000 feet per second by reduction in grain size alone. However, changes in the grain size of the atomized metal to micron size capable of measurement only by special means, such as the photomicrograph, produce unexpected results of a totally different character. When the metal particles reach a micron size as low as 30 microns or less it becomes possible to achieve results of an unexpected and sensational character. Whereas decrease in grain size of explosive particles may change the results in such a way as to amount merely to a difference in degree I find that in the case of atomized metal of sub-sieve micron size there is an unexpected and sharp transition point where the velocity of an explosive increases abruptly. This is well illustrated by the graphs in Figs. 1, 2, 3 and 4.

Referring first to Fig. 1, this graph represents the results of tests made on a composition having the following formula:

Example 1

	Per cent
Ammonium nitrate-----	55.0
Sodium nitrate-----	39.0
Calcium stearate-----	.5
Atomized aluminum-----	2.5
Wood pulp-----	2.0
D. N. T. oily-----	1.0

This graph was plotted after a series of tests made with compositions having the formula of Example 1. The plotting points represent successive tests made where only the grain size of the metal was changed.

The charges were each exposed to the impact of standard #6 commercial blasting cap. When the mean grain size of the atomized aluminum was 40 microns the charge did not fire. Again when the mean grain size was about 14 microns the charge did not fire. When, however, the mean grain size reached about 12 microns the charge fired with a velocity of detonation of about 7,400 feet per second. As the grain size was further reduced the velocity was increased as high as about 7,800 feet per second. Thus it is apparent that with any formula including atomized aluminum or an equivalent metal there is a critical point at which detonation becomes possible for some grain size in the lower micron ranges and I have found this to be 30 microns or less.

The following formula was tested in a manner similar to that just described with the results indicated in Fig. 2.

Example 2

	Per cent
Sodium nitrate-----	57.5
Ammonium nitrate-----	35.0
Atomized aluminum-----	3.5
Wood pulp-----	2.0
D. N. T. oily-----	2.0

Here the critical point was at 30 microns.

Tests of still another formula designated Example 3 below, gave the results shown in Fig. 3.

Example 3

	Per cent
Potassium nitrate.....	58.0
Ammonium nitrate.....	35.0
Atomized aluminum.....	3.5
Wood pulp.....	2.0
D. N. T. oily.....	1.5

In the example of Fig. 3 the transition occurred when the metal particles had a size of about 17 microns.

Examples 1, 2 and 3 referred to above are concerned with compositions containing a mixture of nitrates. The critical effects of changing the grain size are even more striking when atomized metal is mixed with ammonium nitrate only, and progressive changes are made in the amount of and in the grain size of the metal.

The following table shows the results of tests on compositions composed of ammonium nitrate and atomized aluminum alone:

Example 4

	NH ₄ NO ₃	Al	Grain size of Al	
	Per cent	Per cent		
Test #1.....	96	4	-325 mesh..	Incomplete detonation.
Test #2.....	90	10	-325 mesh..	Do.
Test #3.....	85	15	-325 mesh..	Do.
Test #4.....	80	20	-325 mesh..	Do.
Test #5.....	75	25	-325 mesh..	Do.
Test #6.....	96	4	1-12 microns.	Complete detonation.

In the above table six tests were made in succession on mixtures of ammonium nitrate of the same characteristics throughout, with the amount varied in accordance with changes in the amount of powdered aluminum used. The mixtures were all loaded at shaking density in 1 1/8" by 8" paper cartridges and firing attempted using a standard #6 blasting cap.

Tests 1 through 5 were carried out using powdered aluminum of -325 mesh in which the majority of the particles had a grain size in excess of 30 microns and as large as 44 microns. The amount of aluminum was increased in successive tests from 4% to 25%, as indicated in the table, without obtaining a single complete detonation.

Test #6 was then made using 4% aluminum, as in test #1 but using an average grain size in the range 1-12 microns. Complete detonation was obtained. The graph shown in Fig. 4 is a plot in the form of a curve indicating the critical grain size for the 4% aluminum mixture to be at about 14 microns with a detonation velocity of about 7,100 ft./sec. and correspondingly

greater velocities by decrease in grain size of the aluminum down to 3 microns giving a velocity of about 8,800 ft./sec.

Thus it is apparent that for all nitrate mixtures with atomized aluminum there exists a critical grain size for detonation and that a marked change occurs when the grain size reaches 30 microns or below.

While the amount of atomized metal used may vary considerably with conditions, since it is the particle size that is controlling, it should be present in a percentage of not less than about 1/2 of one per cent of the weight of the nitrate while the percentage of metal may reach as high as 6 per cent of the composition or even more. As indicated above the largest particle should not be larger than 30 microns whereas the smallest particles may be of one micron or less.

This application is a continuation-in-part of my application Ser. No. 696,347, filed September 11, 1946, which is, in turn, a continuation-in-part of my original application Ser. No. 571,959, filed January 8, 1945, now both abandoned.

What is claimed is:

1. A detonating explosive composition free of cap sensitive materials and consisting of ammonium and sodium nitrates 35% to 88%, at least about 35% of which is ammonium nitrate, dinitrotoluene 1% to 8%, carbonaceous combustible material 0.75% to 12% and sufficient nodular atomized aluminum, having a grain size not exceeding 30 microns to cause detonation of the composition by a #6 blasting cap, said aluminum being present in an amount not to exceed about 6% by weight of the composition.

2. A detonating explosive composition free of cap sensitive materials and consisting of about 57.5% sodium nitrate, 35% ammonium nitrate, 2% carbonaceous combustible material, 2% dinitrotoluene and sufficient nodular atomized aluminum having a grain size not exceeding 30 microns to cause detonation of the composition by a #6 blasting cap, said aluminum being present in an amount not exceeding 6% by weight of the composition.

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