UNITED STATES PATENT OFFICE.

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EXPLOSIVE AND PROCESS OF MAKING EXPLOSIVES.

1,371,215. Specification of Letters Patent. Patented Mar. 15, 1921.

No Drawing. Application filed July 14, 1917. Serial No. 180,561.

To all whom it may concern:

Be it known that I, JACOB BARAB, a citizen of the United States, residing at Flushing, county of Queens, and State of New York, have invented certain new and useful Improvements in Explosives and Processes of Making Explosives, fully described and represented in the following specification.

The present invention relates to new explosives and to processes of making explosives.

It has been recognized that nitro-glycerin used in its liquid state has very valuable properties as an explosive, but it has some disadvantages that are so serious as to materially restrict its employment in the liquid state, and even to injuriously affect its value when used in either the dynamite or colloidal forms.

The principal disadvantages of nitro-glycerin and explosive mixtures containing it are that they freeze at a commonly occurring low atmospheric temperature (*e. g.* pure nitro-glycerin melts at 13.3° C.) and that they are relatively sensitive to friction and shock. At high temperatures (180 to 200° C.) liquid nitro-glycerin explodes.

As a result of these disadvantageous properties, the use of the liquid nitro-glycerin in explosives is restricted to those cases where the liquid condition, the quick action, and great strength are so important as to override the dangers due to the disadvantageous properties.

In its broad aspect the present invention comprises an explosive which will remain liquid at all atmospheric temperatures encountered in actual practice, which will be insensitive to friction, relatively insensitive to shock, which will not decompose at, and also will be sufficiently nonvolatile at atmospheric temperatures to be satisfactory for practical purposes. Furthermore, when detonated by a primer, it will be as quick in action and fully as strong as nitro-glycerin.

Such an explosive has all the advantages of liquid nitro-glycerin without its dangerous disadvantages.

The starting material for the new explosive is a propylene glycol product, such, for example, as is made from oil gas by selectively chlorinating the oil gas to form mostly propylene chlorhydrin, and then converting this chlorhydrin into glycol. A process of making such a propylene chlorhydrin is set forth in application Serial No. 178,364 to Byron E. Eldred, filed July 3, 1917.

This particular glycol when suitably nitrated and properly stabilized gives an explosive product which has the properties hereinbefore recited. On analysis, it has substantially the percentage composition of propylene glycol dinitrate, although its physical properties, stated above, particularly distinguish it as an explosive from any nitrated glycols heretofore known to me.

While an explosive having the above recited properties is highly advantageous in practice, it is possible in the best embodiment of the invention to provide an explosive having still further very advantageous properties. For example, I have produced, as a specific embodiment of the invention, a liquid explosive which had the properties shown by the following:

It requires more than sixty minutes to produce the standard coloration on standard potassium iodid starch papers at 71° C., as employed in the Abel heat test.

A drop of this liquid explosive at the end of a capillary tube, when suddenly introduced into a hot flame merely decomposes without exploding.

When subjected to continuous heating with gradually rising temperature, under atmospheric pressure, there was no visible decomposition until about 140° C. Above this temperature, up to 200° C., the product volatilized with decomposition, but at no time during this heating did it decompose with explosive violence.

A few c. c., in a test tube heated over a candle flame entirely volatilized with decomposition, but at no time did it reach explosive violence.

It will withstand a temperature of —40° C. without freezing.

When subjected to a temperature of —50° C. for fifteen to twenty minutes, it becomes somewhat thick or more viscous, but does not become solid and quickly returns to its normal condition with increase of temperature.

The new product is non-hygroscopic and insensitive to friction. It is more insensi-

tive to shock than nitroglycerin, but can be detonated by a relatively weak primer and the detonation appears to be as quick and complete as with nitroglycerin, for tests of the new explosive in both open and closed lead chambers, showed a strength for equal weights, as great as, and in some cases greater, than that of nitroglycerin.

A 30 caliber rifle bullet was fired through a can filled with the new liquid explosive, without exploding it or even igniting the explosive.

A commercial nitroglycol made in accordance with the present invention, had a light straw color, and a specific gravity of 1.38 at 23° C. On analysis, it gave 16.73 per cent. nitrogen.

From the above-mentioned new liquid explosive, a new solid explosive product may be formed. This consists of a mixture of the liquid explosive with a suitable absorbent. In one embodiment of the invention which gave good results, this solid explosive product was made by combining 40 per cent. of the liquid explosive with 44 per cent. sodium nitrate, 15 per cent. of wood pulp and 1 per cent. calcium carbonate.

This new solid explosive mixture was submitted to centrifugal action for five minutes at a rate of six hundred revolutions per minute. The loss of the explosive liquid due to this action, was only two and one-half per cent. This is well within the limit of safety.

The new explosive product has been kept in a loosely covered capsule for two days in a heated oven at 75° C. with a loss due to volatilization of only 3 per cent., and test of the vapor showed no products of decomposition.

This new explosive in solid form when detonated was found to be somewhat more powerful than a 40 per cent. dynamite made with nitroglycerin, and it retains all the valuable properties of the new liquid explosive, in that it is non-freezing and undecomposable at atmospheric temperatures, substantially non-volatile under the general conditions of use, retains the liquid explosive so firmly as to be non-exuding under general conditions of use, and finally is so insensitive to friction as compared with the corresponding nitroglycerin dynamite made in the same way, that on the pendulum friction machine having a steel shoe weighing 20 kilograms arranged to strike against a steel anvil, the new explosive in solid form did not explode and no indication of local cracking produced by the explosive could be noted, even when the pendulum was dropped from a height of 2 meters.

The corresponding nitroglycerin dynamite tested in the same machine exploded every time, even when the pendulum was dropped from a height of only 1½ meters.

Notwithstanding this insensitiveness to friction, the new solid explosive can be detonated satisfactorily by a relatively weak primer. The strength of the new explosive product is somewhat greater than that of the corresponding nitroglycerin dynamite.

Referring again to the liquid explosive, one important and valuable property thereof is that it forms a colloid when mixed with nitrocellulose and the resultant gelatin explosive has valuable properties distinguishing it from nitroglycerin gelatins.

The important differences between this new explosive and explosives containing nitroglycerin, are that the former shows no signs of decomposition under any atmospheric temperatures, nor temperatures up to 75° C.; is much less sensitive to shock; is practically insensitive to friction; does not freeze at any atmospheric temperatures, nor any temperatures down to —50° C.; and at very high temperatures decomposes without exploding. The sensitiveness to shock of the new explosive may be still further reduced by the addition of camphor, as it satisfactorily responds to the latter treatment.

An explosive gelatin was made up as follows:

14 parts of nitrocellulose (showing 12.25% nitrogen), 100 parts of nitrated propylene glycol. This formed a very stiff consistent gel, which under strong pressure and continued standing, showed no signs of exudation. This gel easily detonated when a primer containing three-tenths of a gram of fulminate of mercury was used. In the Trauzl lead block test it produced an expansion of 420 c. c. Picric acid, as well as trinitrotoluol, under similar conditions, produced an expansion of about 215 c. c.

The new process for the manufacture of the new liquid explosive hereinbefore referred to, will now be described.

While this process when applied to the nitration of a propylene glycol of the kind hereinbefore designated results in the valuable liquid explosive described, it is to be understood that this part of the invention is not limited to the use of such propylene glycol, but gives an improved nitrated product when other glycols such as those of ethylene or the butylenes are used as a starting material. For example, although nitrated ethylene glycol has been made heretofore by other processes, it has not been satisfactory for explosive purposes, because of its high volatility and instability under atmospheric conditions.

When, however, it is made in accordance with the present invention, the resultant product, although still somewhat volatile, is much less so than by the old process. Moreover, the glycols when nitrated and stabilized in accordance with the present inven-

tion will endure the Abel heat test at 71° C., a much longer time than when made by previous processes.

The method of nitrating will now be described in its preferred form as applied to the nitration of a propylene glycol, and particularly the propylene glycol obtained as hereinbefore described.

The composition of the acid mixture used for nitrating the glycols may vary greatly; for example:

Water from 0 to 15%
Nitric acid 25 to 50%
Sulfuric acid 50 to 70%.

The quantity of acid used for the nitration is calculated so that from eight to ten per cent. of nitric acid will remain in the spent acid.

One of the acid mixtures used for nitrating was of approximately the following composition, by weight:

Sulfuric acid	61.00%
Nitric acid	36.00%
Water	3.00%
	100.00%

The acid mixture is cooled to about 3° C. and is not allowed to rise above 10° C. during the nitration step.

The glycol is slowly added to the acid mixture, which is kept well stirred, preferably by air agitation.

After all the glycol is added the mixture is allowed to stand for a short time, usually about ten minutes, at a temperature not exceeding 10° C.

On standing, the nitrated glycol separates readily from the acid mixture and rises to the top. The acid mixture is removed, for example, by drawing it off from the bottom, and then the nitrated glycol is subjected to a washing treatment. The first washing is done very thoroughly with water until a test with litmus paper shows the nitrated product to be about neutral. Usually about four washings of water are required, each lasting three to five minutes, carried out with air agitation.

After sufficient washing with water to obtain the desired neutrality, the water being decanted from the nitrated product, the latter is then thoroughly agitated for a few minutes with about an equal weight of a one-fourth per cent. ammonia solution for three minutes.

Then, after the removal of the ammonia wash solution, another washing with water for about three minutes is given.

Then the nitrated product is washed with a stronger ammonia solution, viz., one containing about one-half per cent. ammonia for three minutes. Then another washing with water follows for three minutes. Then another washing with a half per cent. of ammonia solution for five minutes is given. After this, another washing with water for three minutes takes place.

Thereafter follows a washing with a still stronger ammonia solution, viz., one containing about one per cent. of ammonia for about three minutes. Another washing with water for three minutes is given. Then a two per cent. ammonia solution is used for five minutes. This is followed by a thorough washing with water, as, for example, four washes for three to five minutes each.

It will be noted that this washing method involves the use of plain water and ammonia solution in alternation; also, the ammonia solution of the different ammonia washes is increased in strength, a weaker solution being used at first and a stronger solution being used last. When the ammonia solution is of the same strength as the one previously used, the time of treatment is increased. In each case the quantity of wash is about equal in weight to the nitrated product.

The steps recited above are given as best examples for a particular quality of propylene gycol and for the specified acid used. At the same time it is to be understood that the number of alternate washings may be modified depending on the quality of the glycol, the composition of the mixed acid and the temperature of nitration. Also, the strengths of the respective ammonia solutions may be somewhat modified, it being important, however, to begin the ammonia treatment with the weaker solution and to end it with the stronger solution. After this washing treatment along the lines indicated, and the last-mentioned thorough washing with water, the nitrated product is then suitably dried. In the laboratory this is best carried out in a vacuum desiccator over calcium chlorid, in the well known manner, for removal of the last traces of water. After this drying treatment the product is allowed to stand for a considerable time, usually about six days.

After this aging treatment the product is again subjected to washing steps, preferably by first washing with water for three minutes, then with a one per cent. ammonia solution for three minutes, again with water for three minutes, and then with a two per cent. ammonia solution for five minutes, after which the product is thoroughly washed with water four or five times for three to five minutes at a wash.

After this, the product is washed with a borax solution, which should be of about two per cent. strength, for about five minutes.

Finally, the product is washed with water for about five minutes, and then is dried in the vacuum desiccator, as before. This gives the liquid explosive product. When

the propylene glycol hereinbefore described is employed as a starting material, the resultant explosive product will have the valuable properties hereinbefore described.

One important feature of the new liquid explosive is that it requires less nitric acid to nitrate its starting material than does nitroglycerin. In general terms, it may be said that nitroglycerin requires 24% more nitric acid for its nitration than does the new liquid.

What is claimed is:

1. An explosive, liquid at all atmospheric temperatures, and insensitive to friction in the standard pendulum testing machine, substantially as described, said explosive comprising an olefin glycol dinitrate.

2. An explosive, liquid at all atmospheric temperatures, insensitive to friction in the standard pendulum testing machine, substantially as described, and which explosive is non-hygroscopic, said explosive comprising an olefin glycol dinitrate.

3. An explosive, liquid at all atmospheric temperatures insensitive to friction in the standard pendulum testing machine, substantially as described, and when detonated having substantially the strength of nitroglycerin, said explosive comprising an olefin glycol dinitrate.

4. The new explosive product which has substantially the percentage composition of propylene glycol dinitrate, which is non-hygroscopic, endures the Abel heat test at 71° C. for more than an hour, which decomposes only above 140° C., freezes below —40° C., and a drop of which when suddenly introduced into a flame decomposes without exploding.

5. An explosive in solid form, comprising an absorbent and a liquid explosive having substantially the percentage composition of a nitrated propylene glycol, said solid explosive being non-freezing and non-decomposing at atmospheric temperatures, and losing not to exceed 3 per cent. by weight on centrifuging at 600 revolutions per minute.

6. An explosive in solid form, comprising an absorbent and a liquid explosive having substantially the percentage composition of a nitrated propylene glycol, said solid explosive being non-freezing and non-decomposing at atmospheric temperatures, which loses not more than 3 per cent. of its weight on heating for 48 hours at 75° C., and losing not to exceed 3 per cent. by weight on centrifuging at 600 revolutions per minute.

7. A colloidal explosive comprising nitrocellulose and a liquid explosive having substantially the percentage composition of propylene glycol dinitrate.

8. The new explosive which has substantially the percentage composition of propylene glycol dinitrate, said explosive being liquid at all atmospheric temperatures and insensitive to friction in the standard pendulum testing machine, substantially as described.

9. The process of producing nitrated glycols, which consists in subjecting the glycol to the action of a mixture comprising nitric and sulfuric acids, then washing the nitrated product alternately with water and with ammonia solutions, and drying it.

10. The process of producing nitrated organic compounds, which consists in subjecting the compound to be nitrated to the action of a mixture comprising nitric and sulfuric acids, then washing and drying the nitrated product, then aging it, and again washing and drying it after such aging.

11. The step in the process of nitrating glycols, which consists in subjecting the glycol to the action of a mixture comprising nitric and sulfuric acids, washing the nitrated product, and finally subjecting the product to the action of a solution of borax, and then washing and drying it.

12. The process of producing nitrated organic compounds, which consists in subjecting the compound to be nitrated to the action of a mixture comprising nitric and sulfuric acids, then washing and drying the nitrated product, then aging it, thereafter submitting it to the action of a solution of borax, and then washing and drying it.

13. The process of nitrating glycols, which consists in subjecting the compound to the action of a mixture comprising nitric and sulfuric acids, then washing the nitrated product alternately with water and solutions of ammonia, the ammonia solutions employed being weakest at first and strongest at the end, thoroughly washing the nitrated product with water, and drying it.

In testimony whereof I have hereunto set my hand.

JACOB BARAB.