UNITED STATES PATENT OFFICE.

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NITROGLYCOLS.

1,307,032. Specification of Letters Patent. Patented June 17, 1919.

No Drawing. Application filed July 24, 1918. Serial No. 246,452.

To all whom it may concern:

Be it known that I, JACOB BARAB, a citizen of the United States, residing at Dover, county of Morris, and State of New Jersey, have invented a new and useful Improvement in Nitroglycols, of which the following is a full, clear, and exact description.

In an application filed by me July 18, 1917, Serial No. 180,561, I set forth a new liquid explosive having substantially the percentage composition of propylene glycol dinitrate which is comparable in strength, quickness of action and capacity of absorption in a porous carrier, to nitroglycerin, but which possesses certain valuable properties, such as an extremely low freezing point, insensitiveness to friction and heat, and relative insensitiveness to shock, which are not possessed by nitroglycerin, and which render it safely available, in its liquid state, as an explosive, under conditions that would render the use of nitroglycerin very dangerous or even prohibitive. While propylene glycol dinitrate is sufficiently non-volatile at atmospheric temperatures to be satisfactory for practical use, it is clear that an explosive having the other qualities of nitrated propylene glycol, but possessed of a substantially lower volatility, would be of great practical advantage. My invention comprises an explosive of this character.

I have discovered that nitrated trimethylene glycol possesses all the valuable qualities of nitrated propylene glycol and exhibits, in a pronounced degree, the other quality sought, namely: comparatively low volatility.

While trimethylene glycol has the same percentage composition as propylene glycol, and while the percentage compositions of the nitrated products are the same, the two glycols are produced from entirely different sources, and the two glycols, as well as the two nitrated products, are expressed by different formulæ and have different physical and chemical characteristics.

The formula for propylene glycol is:

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_3 \end{array}$$

While that for trimethylene glycol is:

$$\begin{array}{l} CH_2OH \\ | \\ CH_2 \\ | \\ CH_2OH \end{array}$$

The formula for nitrated propylene glycol is:

$$\begin{array}{l} CH_2NO_3 \\ | \\ CHNO_3 \\ | \\ CH_3 \end{array}$$

While that for nitrated trimethylene glycol is:

$$\begin{array}{l} CH_2NO_3 \\ | \\ CH_2 \\ | \\ CH_2NO_3 \end{array}$$

It will be noted, from the above formulæ, that in propylene glycol the OH radicals are adjacent, while in trimethylene glycol the OH radicals are attached to the end carbons. Comparing the formulæ for the nitrated products, the same difference exists with respect to the NO_3 radical.

The following differences in the physical properties of the two glycols may be emphasized. The boiling point of propylene glycol is about 188 degrees C., while the boiling point of trimethylene glycol is about 206 degrees C. At 23 degrees C., the specific gravity of propylene glycol is 1.0384, while the specific gravity of trimethylene glycol is 1.0672. Differences of less importance are: trimethylene glycol is a darker yellow, propylene glycol being almost or quite colorless. Both have a bitter sweet taste, but the bitterness of propylene glycol is relatively and actually slight.

The only practicable commercial way of producing propylene glycol is by the cracking of oil gas followed by a recently discovered effective means of chlorinating the unsaturated derivatives (practically wholly propylene and ethylene) to chlorhydrins and making the glycols from the chlorhydrins. Trimethylene glycol, however, is a by-product in the manufacture of glycerin from cotton-seed oil.

Comparing the nitrated products: The specific gravity of nitrated propylene glycol is 1.38 at 15 degrees C., its color is a pale yellow, and it has a prounounced ethereal odor. The specific gravity of nitrated trimethylene glycol is 1.43 at 27 degrees C., and it has a deep yellow color and a faint ethereal odor. The most pronounced difference is in their relative volatilities. Taking nitrated propylene glycol as a standard for volatility, nitrated trimethylene glycol is only about 37½ per cent. volatile.

Thus, different samples of ten grams of

nitrated trimethylene glycol were exposed to the air in weighing bottles of about 20 sq. cm. cross-section. The loss in weight, at the end of four days, was from .30 to .40 per cent. At the end of eleven days, the further loss was about one per cent. At the end of eighteen days, a further loss of about one-half of one per cent. occurred. During the next ten days, the loss was about four-fifths of one per cent. At the end of the twenty-eight day period, the total loss was from 2.6 to 2.7 per cent. With corresponding samples of nitrated propylene glycol, the loss approximated 7 per cent.

Similar comparative volatility tests were made of samples of each of the explosives absorbed in one of the standard absorbents for nitroglycerin, namely: 14 per cent. of wood pulp, 45 per cent. sodium nitrate and one per cent. chalk, the remaining 40 per cent. being the liquid explosive. The test continued for three days, at the end of which time the loss in weight of the nitrated propylene glycol powder was about 1.52 per cent., while the nitrated trimethylene glycol powder had lost about .59 per cent. in weight.

Samples of the two liquid explosives, heated slowly in test tubes immersed in a paraffin bath, behaved quite differently. While nitrated trimethylene glycol began to boil at a lower temperature than nitrated propylene glycol (148° C. as compared with 180° C.), the latter completely evaporated during a rise of temperature through a further range of about 5° C., whereas the former was raised in temperature about 50° C. before it evaporated to dryness. Nitroglycerin started to boil, under the same conditions, at about 145° C. and exploded at 218° C.

In other essential respects the two products have similar characteristics. Upon subjection to extreme cold, nitrated propylene glycol becomes slightly viscous at —44° C., is very viscous at —68° C., and is extremely stiff at —77° C. Nitrated trimethylene glycol becomes slightly viscous at —31° C., is very thick at —53° C. and solidifies at —57° C. These figures are approximate only, the slowness and gradualness of the passage of the liquid from fluidity to slight viscosity and thence to extreme viscosity and solidification making exact accuracy difficult. In regard to low freezing point, the theoretical advantage is with nitrated propylene glycol, but the freezing point, or even the temperature at which viscosity is measurable, is so low that, for all practical purposes, the two explosives are equally valuable in respect of their non-freezing qualities.

Not only is nitrated trimethylene glycol, as compared with nitrated propylene glycol, of low volatility, but the spent acids from the former product are more or less unstable if allowed to stand without agitation. The spent acids from nitrated trimethylene glycol are perfectly stable.

Trimethylene glycol may be nitrated by the known method most usually employed for nitrating glycerin, with the following modifications: In view of the lower specific gravity of the glycol, more vigorous agitation is required. A smaller proportion of nitric acid will suffice, about 166 pounds of nitric acid being required for 100 pounds of trimethylene glycol, while 205 pounds of nitric acid are required for 100 pounds of glycerin.

Instead of washing alternately with water and sodium carbonate solution, the washing should be with pure water, although alternate washing with weak ammonia is permissible. The use of sodium carbonate must be avoided. An extremely small quantity of sodium carbonate might not be harmful, but it would be without utility, and close adherence to the method in vogue for purifying nitroglycerin would not result in a satisfactory product.

The specific process of nitrating propylene glycol, as set forth in my said application, may be advantageously used in the nitration of trimethylene glycol, but as this process is not herein claimed, it need not be specifically set forth. No difficulty in stabilizing nitrated trimethylene glycol is encountered if the product is thoroughly washed. However, nitrated trimethylene glycol may be purified with pure water, as above stated, while the purification of nitrated propylene glycol requires the use of a weak ammonia solution.

Like nitrated propylene glycol, nitrated trimethylene glycol is non-hygroscopic, endures the Abel heat test at 71° C. for more than an hour, decomposes above 140 degrees C., does not explode when a drop is introduced suddenly into a flame, remains liquid at atmospheric temperatures, is insensitive to friction, is relatively insensitive to shock, and is absorbable in the ordinary absorbents to approximately the same degree.

When absorbed in any of the usual absorbents employed in the manufacture of dynamite, the new explosive, like nitrated propylene glycol, retains all its valuable qualities, and is non-exuding under general conditions of use.

Notwithstanding the insensitiveness to friction of the solid explosive, it can be detonated satisfactorily by means of a weak primer.

Another valuable quality of the liquid explosive is that it forms a colloid when mixed with nitrocellulose and the resultant gelatin explosive has valuable properties distinguishing it from nitrogylcerin gelatins. A satisfactory composition comprises 14 parts

of nitrocellulose (showing 12.25 per cent. nitrogen) and 100 parts of nitrated trimethylene glycol.

While I have herein described the product trimethylene glycol dinitrate and its process of manufacture, there may also be present in appreciable quantities, the mononitrate and, therefore, in claiming the nitrated product, I do not mean to be limited to the pure dinitrate.

It will also be understood that the nitrated product forming the subject-matter of this patent may be added to nitroglycerin in different proportions for the purpose of producing what may be called either a modified nitrated trimethylene glycol or a modified nitroglycerin. For example, if nitrated trimethylene glycol be added to nitroglycerin, it will lower the latter's freezing point to a degree dependent upon the percentage of the addition and will render the nitroglycerin less sensitive to heat, friction and shock.

The new explosive may also be used in admixture with nitro-compounds, as, for example, trinitrotoluol or trinitrotoluol oils.

Having now fully described my invention, what I claim and desire to protect by Letters Patent is:

1. The new explosive product which has substantially the percentage composition and molecular arrangement of trimethylene glycol dinitrate.

2. The new explosive product having substantially the formula:

$$\begin{array}{l} CH_2NO_3 \\ | \\ CH_2 \\ | \\ CH_2NO_3 \end{array}$$

3. The new explosive product which has the percentage composition of propylene glycol dinitrate but which differs therefrom in that the NO_3 radicals are attached to the end carbons and whose volatility is less than one-half that of propylene glycol dinitrate.

4. The new explosive product which has the percentage composition of propylene glycol dinitrate but which differs therefrom in that the NO_3 radicals are attached to the end carbons and which has a higher specific gravity, a higher boiling point, and is substantially less volatile, than nitrated propylene glycol.

5. The new explosive product trimethylene glycol dinitrate whose specific gravity at 27 degrees C. is approximately 1.43.

6. The new explosive product trimethylene glycol dinitrate having approximately the strength of trinitroglycerin and nitrated propylene glycol, which is non-freezing at —40 degrees C., remains liquid and stable within the highest range of atmospheric temperature, does not explode when a drop is suddenly introduced into a flame, is insensitive to friction and relatively insensitive to shock, completely evaporates without explosion when slowly raised in temperature, and which is substantially less volatile than propylene glycol dinitrate.

7. An explosive comprising liquid trimethylene glycol dinitrate and an absorbent.

8. An explosive comprising trimethylene glycol dinitrate, an absorbent and an oxygen carrier.

9. An explosive comprising trimethylene glycol dinitrate and nitroglycerin.

10. A new explosive containing trimethylene glycol dinitrate.

In testimony of which invention, I have hereunto set my hand, at Kenvil, N. J., on this 17 day of July, 1908.

JACOB BARAB.