# UNITED STATES PATENT OFFICE.

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## NITROGLYCOLS.

1,307,034. Specification of Letters Patent. Patented June 17, 1919.

No Drawing. Application filed July 24, 1918. Serial No. 246,454.

*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.

It has been known for years that the glycols, such as ethylene, butylene and propylene, are capable of nitration to produce explosives analogous in their properties to nitroglycerin, and such capacity might be said to be quite obvious in view of the analogous character of glycol and glycerin. Equally obvious, of course, is the possibility of nitrating any mixture of glycols. However, until comparatively recently, the possibilities in this direction have been of only academic interest, because of the impossibility of producing glycols on an economical and commercial scale. Efforts have been made to produce these glycols by cracking oil gas, chlorinating the unsaturated derivatives to chlorhydrins, and making the glycols from the chlorhydrins. The chlorination of these unsaturated derivatives to chlorhydrins presented, for some time, apparently insuperable difficulties. Bringing them in contact with chlorin gas in any known way resulted, so far as any measure of success was attained, in the production of dichlorids, or so-called "Dutch liquid", which could not be successfully converted to glycol. Within a comparatively recent period, however, successful processes have been developed for the chlorination to chlorhydrin of certain of the olefins on a commercial scale, and thus, for the first time, the possibilities of nitrating glycols derived from these olefin chlorhydrins began to assume a practical importance.

It has been assumed that the usual processes in general use for the manufacture of nitroglycerin from glycerin could be applied unchanged to the manufacture of nitroglycol from glycol, but my own exhaustive experiments demonstrated that thereby no explosive could be thus produced that would in any sense meet commercial requirements. Thus, in the purification of the material after nitration, the washing alternately with water and sodium carbonate was found not to be practicable and it was discovered that it was essential to avoid the use of sodium carbonate. I eventually succeeded, however, in nitrating propylene glycol, and my preferred process for so doing is set forth in an application filed by me July 14, 1917, Serial No. 180,561. This propylene glycol dinitrate possesses certain qualities which, in the literature of the art, have been ascribed to nitrated glycols generally or which might have been taken for granted by a chemist possessing ordinary theoretical knowledge of the subject, but it exhibited other qualities without which it would hardly have been available as a substitute for nitroglycerin; and I believe the disclosures of my said application were the first in the art to give such information with respect to the manufacture of a nitroglycol as would enable those skilled in the art to make the explosive without the necessity of independent experimentation. Among the valuable qualities of propylene glycol dinitrate, aside from its very low freezing point, are its relative insensitiveness to friction and shock as demonstrated by the hammer test, its non-hygroscopicity, its very high boiling point, its stability above the highest range of atmospheric temperature, its gradual evaporation without explosion when subjected to a gradual elevation of temperature to an exceedingly high point, its decomposition without exploding when dropped into a flame, and its endurance of the Abel heat test at 71° C. for a prolonged period.

There are certain objections to propylene glycol dinitrate that by no means offset its advantages or constitute a real hindrance to its practicable use but which, if they could be removed even in degree, would enhance the practical value of the explosive. Thus it is much more volatile at atmospheric temperatures than nitroglycerin. Again, its oxygen balance is comparatively low, there being a deficiency of about 29% as compared with the oxygen required to secure ideal conditions of combustion. This deficiency may readily be supplied by adding an oxygen carrier. Thus, when absorbed in wood pulp or other absorbent carrier, the addition of

sodium nitrate, as in the manufacture of dynamite, raises the oxygen balance to the desired point. However, it is obvious that it is desirable, if possible, to produce a nitroglycol whose oxygen balance, without the addition of an oxygen carrier, will be relatively high.

I have made exhaustive experiments with ethylene glycol and have found that the nitrated product possesses qualities analogous to those of nitrated propylene glycol. Thus, like nitrated propylene glycol, when heated in a capillary tube, it burns without explosion, it is stable at the highest range of atmospheric temperature, and it gradually evaporates without explosion when subjected to a gradual elevation of temperature to an exceedingly high point. In certain respects, however, it is not comparable in value to nitrated propylene glycol. Thus, the freezing point of nitrated ethylene glycol is about —18° to —19° C. On the other hand, the freezing point of nitrated propylene glycol is so low that I have not been able to determine it. Upon cooling, no viscosity was observable until about —48° C. was reached, and even at —77° C., while the mass was quite stiff, it had not solidified. Nitrated ethylene glycol can not, therefore, be said to be non-freezing at atmospheric temperatures. In severely cold weather, it would be necessary, in its manufacture, to warm it to prevent freezing. It would possess no practical advantage over nitroglycerin in any climate where below zero (Fahrenheit) temperature is prevalent.

Again, nitrated ethylene glycol can not compare with nitrated propylene glycol with respect to sensitiveness to shock or friction. It is much less sensitive to shock or friction, however, than nitroglycerin, although, when subjected to a severe hammer test, it explodes, like nitroglycerin, whereas propylene glycol dinitrate does not.

Nitrated ethylene glycol, however, has the advantage over nitrated propylene glycol of having no deficiency in oxygen and the secondary advantage of being less volatile.

I have also made exhaustive experiments with trimethylene glycol, which is a by-product in the manufacture of glycerin from cotton-seed oil, and found the nitrated product to possess all the advantages of either nitrated propylene glycol or nitrated ethylene glycol, and to possess one striking advantage of its own, namely: comparatively low volatility. It is not more than three-eighths as volatile as nitrated propylene glycol and about three-sevenths as volatile as nitrated ethylene glycol. Its freezing point, not accurately determinable, is probably between —51° C. and —57° C.—approximating, but not reaching, the low freezing point of nitrated propylene glycol, but still emphatically "non-freezing". I therefore regard nitrated trimethylene glycol as the most satisfactory of all the nitroglycols, and the same forms the subject-matter of a separate application filed July 24, 1918, Serial No. 246,452. The only bar to its general use is the likelihood of a deficient supply. At present the product is cheap and available, but this condition arises from the paucity of the demand rather than the plentifulness of the supply. It is obvious that if nitroglycols are to be manufactured on a scale comparable with that of nitroglycerin, the supply of trimethylene glycol will not be adequate. On the other hand, the prospective supply of glycols made from the chlorhydrins of olefins derived from oil gas will be practically unlimited.

As providing a nitroglycol which will meet all the requirements of insensitiveness to heat and friction, comparative insensitiveness to shock, low freezing point, and non-hygroscopicity, which will be sufficiently non-volatile at atmospheric temperatures to meet exacting requirements, and which can be manufactured from materials which will certainly be available in sufficient quantities, I have conceived a nitroglycol explosive composed of nitrated trimethylene glycol and one or more nitrated glycols derived from oil gas olefins, of which I most decidedly prefer propylene and ethylene. The most economical composition is one in which all three nitrated glycols are present, it being, at least at the present time, more economical and practicable to produce from oil gas a mixture of ethylene and propylene and chlorinate both than to separate the two gases prior to chlorination or in the process of chlorination. Nitrated propylene glycol is preferable to nitrated ethylene glycol because of its very much lower freezing point and its comparatively greater insensitiveness to shock, while nitrated ethylene glycol is preferable to nitrated propylene glycol because it has no oxygen deficiency. The proportions of the several ingredients may be varied dependent upon the dominating qualities which it is desired to impart to the explosive, and such variations are within the scope of my invention.

Nitrated ethylene glycol.
Nitrated trimethylene glycol.

This composition has the lowest oxygen deficiency, and is somewhat the least volatile, of any of the compositions, but its freezing point is not as low, nor is it as insensitive to friction, as any of the compositions containing nitrated propylene glycol. Its disadvantages in these particulars, however, are only relative. With a sufficient proportion of nitrated trimethylene glycol,

its freezing point is sufficiently low to warrant it being designated a "non-freezing" explosive; and friction or shock must be extreme to produce an explosion.

Nitrated propylene glycol.
Nitrated trimethylene glycol.

This composition has a lower freezing point than any of the other compositions and is more insensitive to shock and friction. It has a slight oxygen deficiency and is about seven per cent. more volatile than the first composition specified.

Nitrated ethylene glycol.
Nitrated propylene glycol.
Nitrated trimethylene glycol.

This composition is the preferable one based on practical considerations such as the cheapness and availability of the glycols, as hereinbefore explained. With respect to low freezing point, insensitiveness to heat, shock, and friction, and non-volatility, it represents a mean between the first and second compositions and responds, as a practical matter, to all the requirements.

Nitrated ethylene glycol; 30 per cent.
Nitrated propylene glycol; 30 per cent.
Nitrated butylene glycol; 10 per cent.
Nitrated trimethylene glycol; 30 per cent.

This composition is the least desirable of the several compositions specified, because of the deficiency in oxygen and high volatility of one of the constituents, namely: nitrated butylene glycol. If, however, the proportion of nitrated butylene glycol be maintained sufficiently low, the nitrated trimethylene glycol neutralizes, to some extent, the objections to nitrated butylene glycol, especially as regards the latter's volatility, and the composition constitutes a very fair explosive. The presence of nitrated butylene glycol, however, is inadvisable except where nothing is available in the way of chlorhydrins of olefins derived from oil gas except a mixture of ethylene, propylene and butylene chlorhydrins.

All of these explosives seem to possess greater strength than those produced by the nitration of either of the separate ingredients.

Each of the glycols may be nitrated separately, but it is preferable, on the ground of simplicity, convenience and economy, to nitrate all of them together. The procedure may be the same as in the manufacture of nitroglycerin except in the following particulars: In view of the lower specific gravity of the glycols, more vigorous agitation is required. Less nitric acid is necessary. For example, 100 pounds of a mixture of equal parts of ethylene and trimethylene glycols require about 186 pounds of nitric acid; 100 pounds of a mixture of propylene and trimethylene glycols require about 167 pounds of nitric acid; and 100 pounds of a mixture of propylene, ethylene and trimethylene glycols require about 180 pounds of nitric acid. Instead of washing with water and sodium carbonate, as in the purification of nitroglycerin, the washing should be with water and weak ammonia. Any substantial quantity of sodium carbonate in the washing solution is distinctly harmful. The specific process set forth in my said application covering propylene glycol denitrate and its process of manufacture may be advantageously used. No difficulty in stabilizing the product is encountered if it is thoroughly washed. If the glycols are nitrated separately, I prefer to use the weak ammonia solution only in the washing of the propylene glycol dinitrate, and use pure water in washing the ethylene glycol dinitrate and the trimethylene glycol dinitrate. If the nitrated product does not contain nitrated propylene glycol, I prefer to wash the mixture of nitrated ethylene and trimethylene glycols with water only.

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.

The new explosive may be used in admixture with nitroglycerin and the mixture of nitroglycols and nitroglycerin may be absorbed in any of the standard absorbents for nitroglycerin. For example, when added to nitroglycerin, it lowers the latter's freezing point and renders it less sensitive to heat, friction, and shock.

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 nitroglycerin gelatins. A satisfactory composition comprises 14 parts of nitrocellulose (showing 12.25 per cent. nitrogen) and 100 parts of the new liquid explosive.

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

It will be understood that while I propose to use the dinitrates of the specified glycols, there may be formed, in their manufacture, appreciable quantities of the mononitrates, and, therefore, in claiming my improved product, I do not mean to be limited to the pure dinitrates.

Having now fully described my invention,

what I claim and desire to protect by Letters Patent is:

1. An explosive containing trimethylene glycol dinitrate and a nitrated glycol derivative from an olefin.

2. An explosive containing trimethylene glycol dinitrate, propylene glycol dinitrate and ethylene glycol dinitrate.

3. An explosive containing trimethylene glycol dinitrate and propylene glycol dinitrate.

4. An explosive containing trimethylene glycol dinitrate and ethylene glycol dinitrate.

In testimony of which invention, I have hereunto set my hand, at Kenvil, N. J., on this 17 day of July, 1918.

JACOB BARAB.