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# UNITED STATES PATENT OFFICE.

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## DIETHYLENE GLYCOL DINITRATE AND PROCESS OF PREPARING SAME.

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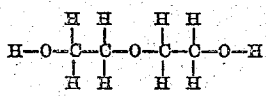
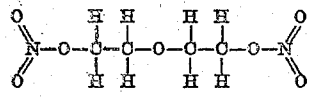
My invention relates to improvements in explosives, and more particularly relates to the preparation of a new and useful explosive compound, diethylene glycol dinitrate, and the use of this compound as a component of explosive compositions. The principal object of my invention is to provide new explosive bodies having desirable properties and which are useful for a variety of purposes.

I have discovered that by the suitable treatment of *66'* dihydroxydiethyl ether, the structural formula of which is



and which is chemically known as dihydroxyl diethyl ether, and which is commonly known as diethylene glycol, I can obtain a liquid body containing from 14.00% to 14.20% of nitrogen, (the theoretical nitrogen content being 14.29%), and which possesses valuable explosive properties.

In these specifications I will refer to the hydroxy ethyl ether of glycol (dihydroxy diethyl ether) by the name diethylene glycol altho recognizing that this name is chemically incorrect as the compound does not possess double bonds characteristic of ethylenic bodies, but instead is a true derivative of ethane and is an aliphatic body possessing no unsaturated valences. I will similarly refer to my new explosive body as diethylene glycol dinitrate, although I also recognize that this term is chemically incorrect and that the body should be more properly described as the nitric acid ester of dihydroxy diethyl ether, the structural formula of my new explosive body being



Diethylene glycol is not a new compound, but has been known for a very long time. Efforts to obtain nitric acid esters of diethylene glycol were made many years ago (Wurtz, Ann. chim. (3), vol. 69, 317-355 (1863) but led to the production of glycolic and oxalic acids instead of the nitric acid ester, this behavior having only recently been explained in the course of my present work, and having been found to be due to a peculiar action of nitric acid as will be now explained.

As a result of a long series of experiments in the nitration of diethylene glycol I have discovered that diethylene glycol dinitrate is unstable at ordinary temperatures in the presence of free nitric acid, and that accordingly the successful nitration of diethylene glycol requires the use of a nitrating mixture of such composition that relatively little or no free nitric acid will be present in the spent acid resulting from the nitration treatment.

I have discovered that by the use of a nitrating mixture containing from 3% to 12% of water, preferably maintained at a temperature lower than 15° centigrade, and of such composition that substantially no free nitric acid is present in the spent acid at the end of the nitration treatment, I can obtain diethylene glycol dinitrate in yields as high as 70% or higher as the crude product and in yields as high as 60% to 65% or higher as the washed product, altho earlier nitration experiments had indicated the production of no diethylene glycol dinitrate from the treatment of diethylene glycol with nitric acid.

As an example of my preferred method of procedure I may take as my nitrating mixture a nitrating acid containing 25% of nitric acid, 67% of sulfuric acid and 8% of water. I preferably cool this nitrating acid to a temperature lower than 15° centigrade, temperatures from 5° centigrade to 10° centigrade being desirable. Purified diethylene glycol is now added to the nitrating acid, in small quantities at a time, and with constant agitation, over a period of thirty minutes, within which period nitration will be found to be substantially complete. By employing a quantity of diethylene glycol just sufficient to completely exhaust the nitric acid originally present in the quantity of nitrating acid used, (this being 21 parts of diethylene glycol to 100 parts of nitrating acid in the example herein given), I find that decomposition of the resulting diethylene glycol dinitrate is so slow that the diethylene glycol dinitrate formed in the nitrating step may be separated from the spent acid by settling, altho the drowning of the spent acid with its contained diethylene glycol dinitrate in a relatively large volume of ice water or a mixture of ice and water is preferable, when the subsequent utilization of the spent acid for denitration purposes is not desired. As a drowning mixture, I prefer to use three parts of a mixture of ice and water to each part by

weight of the nitrated charge from the nitrating operation.

Diethylene glycol dinitrate prepared in accordance with my present invention is a clear, colorless liquid having no perceptible odor. Its specific gravity at 0° centigrade was found to be 1.409 and at 10° centigrade was found to be 1.397. The freezing point of the product is about −11.3° centigrade, altho the liquid may be supercooled without freezing and in one experiment was still liquid at a temperature lower than −30° centigrade.

Diethylene glycol dinitrate is a liquid of notably lower viscosity than nitroglycerin, and admixtures of diethylene glycol dinitrate and nitroglycerin have lower viscosity than nitroglycerin alone. At 15° centigrade the viscosity of diethylene glycol dinitrate in c. g. s. units was found to be 0.099, as compared with a viscosity of nitroglycerin in the same units of 0.511.

At ordinary temperatures I have found diethylene glycol dinitrate to be completely miscible with nitroglycerin and with ethylene glycol dinitrate, and I have discovered that mixtures of diehtylene glycol dinitrate with nitroglycerin, nitropolyglycerin, ethylene glycol dinitrate and with mixtures of nitroglycerin and nitrosugar, possess useful and valuable properties in the manufacture of explosive compositions.

Altho the constitution of diethylene glycol dinitrate would lead to the assumption that the material would have explosive properties, actual tests have indicated the body to have most unusual characteristics in this respect, being so insensitive to detonation as to be unable to produce continuous propagation under conditions which permit nitroglycerin or ethylene glycol dinitrate to readly produce this effect. In admixture with either nitroglycerin or ethylene glycol dinitrate, diethylene glycol dinitrate can be completely detonated and shows an explosive effect but little less than either of the other compounds. As a result of this remarkable behavior I have found it possible to produce a series of useful explosive compositions, by admixing diethylene glycol dinitrate with one or more explosive compounds such as nitroglycerin, nitropolyglycerin, ethylene glycol dinitrate, nitroglucose, nitrosucrose, etc. with or without the presence in the admixture of oxidizing agents such as the nitrates, chlorates or perchlorates of the alkali and the alkali earth metals or equivalent salts of oxidizing nature, and with or without the presence in the admixture of absorbing agents such as wood pulp, ivory nut meal, sawdust, etc. and with or without the presence of anti-acid agents and like substances well known in the explosives art and commonly used in the manufacture of explosives.

Among the very important properties of diethylene glycol dinitrate its low toxicity should be mentioned. Careful tests have indicated that this body possesses much lower toxic action than either nitroglycerin or ethylene glycol dinitrate, and since it has already been pointed out that diethylene glycol dinitrate shows excellent explosive action in admixture with nitroglycerin, it will be evident that by the use of mixtures of nitroglycerin and diethylene glycol dinitrate, or admixtures of diethylene glycol dinitrate with other detonating bodies such as nitropolyglycerin, nitroglycerin-nitrosugar mixtures and nitroglycerin-ethylene glycol dinitrate mixtures, I can desirably modify the sensitiveness and the toxicity of such mixtures while still maintaining substantially the prorata strength of the detonating mixture, the actual explosives strength of diethylene glycol dinitrate being about 65% of the explosive strength of nitroglycerin.

As diethylene glycol dinitrate possesses notably greater viscosity than ethylene glycol dinitrate, but notably lower viscosity than nitroglycerin, it will be evident that the viscosity of ethylene glycol dinitrate may be raised by admixture with diethylene glycol dinitrate, while the viscosity of nitroglycerin may be lowered by such admixture. Accordingly, by the use of suitable proportions of the three materials, desirable control of viscosity may be obtained. The admixture of diethylene glycol dinitrate with ethylene glycol dinitrate is particularly important from a commercial point of view, as the viscosity of ethylene glycol dinitrate is somewhat too low to permit of the liquid being readily held in permanent condition in such absorbents as are readily available in the manufacture of dynamite, without the use of an excessive amount of an absorbent. By admixture of ethylene glycol dinitrate with diethylene glycol dinitrate the viscosity of the ethylene glycol dinitrate is increased, and the resulting explosive, when the mixture is absorbed in wood pulp or like material, shows notably reduced tendency to "leakage" of the liquid explosive ingredient.

Another particularly valuable property of diethylene glycol dinitrate is its ability to reduce the freezing point of introglycerin and of mixtures of nitroglycerin with other materials such as ethylene glycol dinitrate, nitropolyglycerin, liquid trinitrotoluene, nitroglusose, nitrosesucrose and the like. As the freezing of nitroglycerin at temperatures commonly met with under winter conditions is one of its points of greatest disadvantage, mixtures of diethylene glycol dinitrate with nitroglycerin, either alone or in admixture with other bodies, are particularly useful in the preparation of "low freeze" dynamite and similar high explosive mixtures of a liquid detonating agent with a solid absorbing agent, with or without the presence of oxidizing salts and like materials.

From the above it will be evident that my new product diethylene glycol dinitrate has valuable explosive properties in admixture with a large number of other bodies such as are now commonly used in the manufacture of explosives. Because of the wide field of usefulness of my new body in the formulation of explosive mixtures, I will not specify any particular mixture in which it may be used, as in general it may be used, preferably in admixture with nitroglycerin, in substantially all of the explosives in which nitroglycerin is now used, and in substantially equal amounts. I find that a mixture of 5% of diethylene glycol dinitrate, 10% of ethylene glycol dinitrate, 20% of nitrosugar and 65% of nitroglycerin may be used as the equivalent of nitroglycerin in the manufacture of dynamite, low-flame coal mining explosives, smokeless powder, blasting gelatin, ammonia dynamite, gelatin dynamite, and the like, in substantially the same way that nitroglycerin is now used, while the admixture named possesses the desirable property of giving an explosive which resists freezing to a much greater extent than the corresponding explosives made with nitroglycerin alone.

It will be evident from the above that my present invention is of wide applicability and great usefulness, and that many modifications may be made without departing from the essential principles of the disclosure as herein made, and accordingly no limitations should be placed upon my invention, except as indicated in the appended claims.

I claim:

1. The new compound diethylene glycol dinitrate.

2. The process of preparing diethylene glycol dinitrate which comprises admixing diethylene glycol and a mixture of sulfuric acid, nitric acid and water, the nitric acid being present to only the extent theoretically necessary to transform the diethylene glycol to diethylene glycol dinitrate.

3. The process of preparing diethylene glycol dinitrate which comprises admixing diethylene glycol and a mixture of sulfuric acid, nitric acid and water, the nitric acid being present to only the extent theoretically necessary to transform the diethylene glycol to diethylene glycol dinitrate, and maintaining the temperature lower than 15°. centigrade during the nitration treatment.

4. The process of preparing diethylene glycol dinitrate which comprises mixing diethylene glycol with a nitrating mixture containing less than 30% of nitric acid and less than 75% of sulfuric acid and more than 3% of water.

5. The process of preparing diethylene glycol dinitrate which comprises mixing diethylene glycol with a nitrating mixture containing less than 30% of nitric acid and less than 75% of sulfuric acid and more than 3% of water at a temperature lower than 15° centigrade.

In testimony whereof, I have hereunto subscribed my name this 25th day of May, 1927.

WM. H. RINKENBACH.