

# UNITED STATES PATENT OFFICE.

EDMUND VON HERZ, OF CHARLOTTENBURG, GERMANY.

## EXPLOSIVE.

1,402,693.

Specification of Letters Patent.

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No Drawing.

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*To all whom it may concern:*

Be it known that EDMUND VON HERZ, a citizen of Germany, residing at 29 Sybelstrasse, Charlottenburg, Germany, formerly of 48 Schoubergerstrasse, Vienna, Austria, has invented certain new and useful Improvements Relating to Explosives, (for which I have filed an application in Austria, Jan. 25, 1919,) of which the following is a specification.

The well known nitro explosives used in practice belong both as regards their chemical constitution and also their properties and effects in general to two different groups, viz. the ethereal salts of nitric acid and the nitro compounds proper. Typical representatives of the first class are nitro glycerine and guncotton, of the second the aromatic nitro compounds such as trinitrotoluene, picric acid and tetranitromethylaniline. The most prominent features of the ethereal salts of nitric acid are on the favourable side the high amount of energy they contain and on the unfavourable side their easy liability to decomposition and their extraordinarily great sensitiveness towards mechanical influences. In contradistinction hereto is the behaviour of the aromatic nitro compounds. Their advantages are in particular their extraordinary chemical stability and their marked non-sensitiveness towards shock, but their disadvantage is their comparatively low energy.

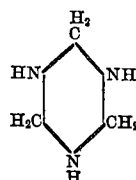
These oppositely contracted properties explain the various attempts which have been made to provide an explosive, which shall combine in itself only the advantages of both classes of explosive, that is to say a compound, which, in addition to the stability and non-sensitiveness of the aromatic nitro compounds exhibits the degree of energy of the ethereal salts of nitric acid. As a result of these attempts hitherto obtained, certain tetranitrated benzene derivatives with the only recently prepared tetranitraniline are the chief. These compounds are most certainly an advance in this direction, but they have not fulfilled the expectations demanded of them, because, as it was subsequently found, the increase in energy conferred by the fourth nitro group was obtained at the expense of a serious decrease in their stability. Owing to a decided liability of the fourth nitro group, which is situated in the meta position, these highly

nitrated substances are so liable to decomposition, that any practical use thereof is not to be thought of.

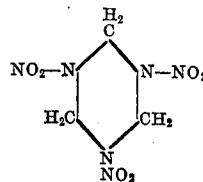
In this way therefore the end aimed at cannot be attained and there are consequently at present no prospects of the realization of this idea.

Now according to the present invention it has been found that hexamethylenetetramine, the well known condensation product obtained from formaldehyde and ammonia, yields, when suitably treated with concentrated nitric acid, an extraordinarily powerful explosive compound, which combines in itself in an absolutely ideal manner the favourable properties of the ethereal salts of nitric acid and the aromatic nitro compounds.

This new explosive substance is neither an ethereal salt of nitric acid nor a pure nitro compound, but is a nitramine with a peculiar ring formation. As chemical investigation has shown, it is derived like hexamethylenetetramine from the hypothetical cyclotrimethylenetriamine



and possesses the following structural formula:



This cyclotrimethylenetrinitramine is formed from all the accessible derivatives of cyclotrimethylenetriamine by the action of concentrated nitric acid. For its production on a large scale, however, only cyclotrimethylenetrimethyltriamine, that is the condensation product obtained from formaldehyde with methylamine could be entertained as a raw material in addition to the already known hexamethylenetetramine, as the other derivatives are difficultly accessible and therefore not economical.

The following method of preparation has

been found to answer well by reason of its good yield and the remarkable uniformity of the product:

Into 500 grms. of nitric acid of a specific gravity of 1.52 freed as completely as possible from nitrous gases are introduced, at first in quite small portions, and gradually, 70 grms. of well dried crude hexamethylenetetramine with continuous stirring. The temperature is kept between 20° and 30° C. during the nitration. After the addition of the hexamethylenetetramine is complete the mixture is allowed to stand for a few minutes at the said temperature and then the mixture is slowly heated to 55° C. By continuous stirring and cooling if necessary the temperature is kept between 50° and 55° for a period of about 5 minutes after which the mass is again cooled down to the original temperature. After 15 minutes standing it is diluted whilst being again cooled by the quite gradual addition of from 3 to 4 times its volume of water and after some time the separated nitro compound is separated from the liquid. After being washed several times with cold water, hot dilute soda solution and again with water it is finally dried at any desired temperature. If necessary the product may also be recrystallized from acetone.

The cyclotrimethylenetrinitramine obtained in this way is a brilliantly white, odourless and tasteless rather coarsely crystalline powder of a neutral reaction. It melts at 200° C. and only detonates at higher temperatures. It is quite insoluble in water, difficultly soluble in hot alcohol more easily so in acetone glacial acetic acid and concentrated nitric acid from which substances it can also be recrystallized.

The cyclotrimethylenetrinitramine is not attacked by either boiling water nor by hot dilute acids and exhibits when subjected to the usual hot storage tests even at unusually high temperatures quite a remarkable stability. It is extraordinarily non-sensitive towards shock, blows and friction and in this respect is about equal to the aromatic trinitro compounds. When ignited it burns slowly without exploding with a bright reddish flame and a fizzing noise like tetranitraniline and leaves no residue.

The most surprising feature of this compound however is its extraordinary explosive and shattering power. In this respect the cyclotrimethylenetrinitramine exceeds all the explosive substances hitherto known, both the enormously energetic nitroglycerine and also the rapidly detonating tetranitraniline. This property it owes, in addition to a composition which permits of fairly complete internal combustion, to its high endothermic character principally. Whereas the formation of the most of the nitro explosives takes place with frequently a consid-

erable loss of energy, the welding together of the cyclotrimethylenetrinitramine from the elements requires the astonishingly high amount of 81.4 calories per molecule. This latent fixed energy is again manifested on explosive decomposition and increases the amount of energy of this explosive to an unusually high amount. Hand in hand with this increase of energy there appears to be also the velocity of detonation which is greater than that of any other known explosive substance. Since there is added as a third factor an extremely large volume of gas due to the large amount of nitrogen and hydrogen contained, this new explosive seems to be of quite enormous effect, which is also clearly shown actually by the surprising results of the lead block and penetration tests.

Another requirement, which is demanded of a good explosive, that of a high density, is possessed by cyclotrimethylenetrinitramine in quite a remarkable degree. The absolute specific gravity is 1.82 and this is a maximum not possessed by any nitro compound hitherto. This fact enables very high loading densities to be obtained which is of great importance for many purposes, e. g., bursting charges for projectiles, detonators and percussion caps.

The following table will show the comparison of all these constants of explosive science with those of other explosives.

Kinds of explosive.	Vol. of gas per kilo-gram litre.	Heat of explosion per kilo-gram caloric (water gaseous).	Speed of detonation at max. density (in per sec.).	Abs. spec. gravity.	Density at a pressure of 350 kg. c. m. <sup>2</sup>
Trinitrotoluene .....	885	680	6,770	1.62	1.40
Picric acid.....	877	778	7,110	1.74	1.42
Tetranitromethylaniline.....	932	968	7,850	1.728	1.50
Tetranitroaniline.....	817	1,073	7,930	1.76	.....
Nitroglycerine.....	712	1,491	8,080	1.6	.....
Cyclotrimethylenetrinitramine.....	905	1,597	8,500	1.82	1.60

A point of importance which is not to be underestimated is also the behaviour of cyclotrimethylenetrinitramine in a sanitary direction. In contradistinction to most of the other nitro compounds it is absolutely non-poisonous, has no tinctorial properties, is completely odourless and tasteless and does not cause either in the form of dust or solution any irritant affections of the respiratory organs and the skin. Injuries to the work people by the usual discolourations of the skin, injurious action on the sense of taste, eruptions, headaches and easy chronic poisoning which are caused in the preparation and handling of the nitro compounds are therefore precluded and the complicated hygienic precautions hitherto necessary become partially superfluous.

From these remarks it will therefore be

clear, that in cyclotrimethylenetrinitramine we have a perfectly new, hitherto unknown explosive, which combines in itself in an ideal way the advantages both of the ethereal salts of nitric acid and also those of the aromatic nitro compounds, combined with remarkable stability and non-sensitiveness while it surpasses all hitherto known and practically usable explosives in energy, shattering power and density and combines with these extraordinary properties in an explosive respect many advantages also as regards sanitary conditions.

Its possibilities of use embrace in respect of the large number of excellent properties which it possesses, all branches of civil and military explosive science. In addition to its use for bursting charges for projectiles, mines, and the like, and as a blasting agent for all mining and mineralogical purposes it is particularly suitable for the production of

extraordinarily rapidly acting detonating fuses and in conjunction with initial means of ignition for the filling of percussion caps, detonators and fuses for projectiles. According to the use for which it is required and the effect aimed at the cyclotrimethylenetrinitramine may be used alone, or in conjunction with or mixed with other explosives or components of explosives.

What I claim and desire to secure by Letters Patent of the United States is:— °

1. An explosive device consisting of a hollow body, containing an explosive comprising cyclotrimethylenetrinitramine.

2. A detonator cap comprising cyclotrimethylenetrinitramine.

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Witnesses:

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