

PATENT SPECIFICATION

145,791

Convention Date (Austria): Jan. 25, 1919.

Application Date (in United Kingdom): July 2, 1920. No. 18,183/20.

Complete Accepted: Mar. 17, 1921.



COMPLETE SPECIFICATION.

Improvements relating to Explosives.

I, EDMUND VON HERZ, a citizen of Austria, of 29, Sybelstrasse, Charlottenburg, Germany, formerly of 48, Schonbergerstrasse, Vienna, Austria, do hereby
5 declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

10 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
15 different groups, *viz.* the ethereal salts of nitric acid and the nitro compounds proper. Typical representatives of the first class are nitro glycerine and gun-
20 cotton, of the second the aromatic nitro compounds such as trinitrotoluene, picric acid and tetranitromethylaniline. The most prominent features of the ethereal
25 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
30 their extraordinarily great sensitiveness towards mechanical influences. In contradistinction hereto is the behaviour of the aromatic nitro compounds. Their
35 advantages are in particular their extraordinary chemical stability and their marked non-sensitiveness towards shock, but their disadvantage is their comparatively low energy.

40 These oppositely contrasted 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
45 hitherto obtained, certain tetranitrated benzene derivatives with the only recently prepared tetranitraniline are the chief. These compounds are most
50 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
55 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
60 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
65 realisation of this idea.

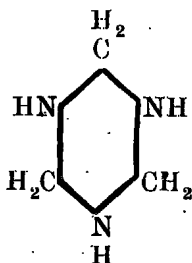
Now according to the present invention it has been found that hexamethylenetetramine, the well known condensation
70 product obtained from formaldehyde and ammonia, yields, when suitably treated with concentrated nitric acid, an extraordinarily powerful explosive compound, which combines in itself in an absolutely
75 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
80 investigation has shown, it is derived like

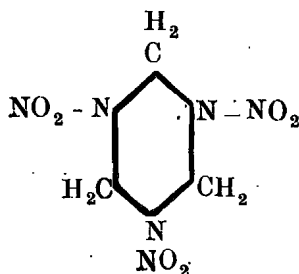
[Price 1/-]



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 recrystallised 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 recrystallised.

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 most of the nitro explosives takes place with frequently a considerable loss of energy, the welding together of the cyclotrimethylene-trinitramine 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 shewn 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 shew the comparison of all these constants of explosive science with those of other explosives.

Kinds of explosive.	Vol: of gas per kilogram litre.	Heat of explosion	Speed of detonation	Abs: Spec. gravity.	Density
		per gram (water gaseous).	at max: (in per sec:)		at a pressure of 550 Kg.c.m. ²
Trinitro toluene - - -	885	680	6770	1.62	1.40
Picric acid - - -	877	778	7110	1.74	1.42
Tetranitromethylaniline -	932	868	7850	1.728	1.50
Tetranitroaniline - -	817	1073	7930	1.76	—
Nitro glycerine - - -	712	1491	8080	1.6	—
Cyclotrimethylene-trinitramine - - -	905	1597	8500	1.82	1.60

A point of importance which is not to be under estimated 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, or mines, 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.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is: -

1. Process for the manufacture of explosives characterised by the fact that hexamethylenetetramine or other derivatives of cyclotrimethylenetriamine are subjected to nitration.

2. An explosive produced by the process according to Claim 1 consisting of cyclotrimethylenetrinitramine by itself alone or in conjunction with or mixed with other explosives or components of explosives.

3. An explosive comprising of cyclo-trimethylenetrinitramine in conjunction with or mixed with other explosives or components of explosives.
- 5 4. The use of explosives herein claimed particularly for bursting charges for projectiles or mines, for the production of blasting agents for mineralogical and mining purposes, for detonating fuses,
- 10 and in conjunction with initial means of

ignition for the filling of percussion caps, detonators and fuses for projectiles.

Dated this 1st day of July, 1920.

HASELTINE, LAKE & Co.,
28, Southampton Buildings, London, 15
England, and
55, Liberty Street, New York City,
U.S.A.,
Agents for the Applicant.

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcomson, Ltd.—1921.