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The following component part numbers comprise the compilation report:

ADP010583 thru ADP010608

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CONVERSION OF HIGH EXPLOSIVES

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An affordable and short-term solution to destroy the high explosives of unexploded ordnance is burning them.

Military high explosives are realized to provide a propellant (propulsion) or a destructive effect (detonation) in munition. The commonly used high explosives can be seen in the summary of fig. 1. High explosives, rocket propellants or propellant powders hardly ever contain pure high explosives. Normally there are mixtures which have to be split up into their individual components when preparing them for conversion. This is relatively simple in the case of high explosive charges (fig. 2) and still feasible for single base propellants but very difficult for double base propellants as they are available in form of solid propellant mixtures. Dissolving and separation of such propellants are very expensive and take much time.

The idea of disposing of or converting high explosives into harmless products first occurred in 1989, after Germany's reunification, when the annuated high explosives stored in the former GDR turned out to be available in enormous quantities. About 300,000 tons of ammunition had to be disposed of. The ammunition did not fulfill Western safety standards and, according to international standards, had been stored for too long (fig. 3).

The disposal procedure which the German Armed Forces used to apply was disassembly of the munitions, which means that they separated the high explosives from the metal parts and then crushed them to burn them in the open air. This combustion is uncontrolled and entails considerable immission of harmful matter in the air, most of all nitrogen monoxide.

Demilitarisation means in this case classification of the ammunition, removal of detonators and H.E. charge.

For the removed H.E. charges, there are different possibilities, e.g. recycling, chemical conversion into valuable products, see fig. 4.

In the chemical point of view, most of the explosives are highly nitrated aromatic compounds, highly nitrated heterocycles or nitric acid esters. Due to the multitude in reactive families, the old high explosives were clearly regarded valuable raw material for chemical synthesis.

Technical reactions are in most cases reduction, oxidation or hydrolysis of a molecule. In the case of nitroaromates, only the reduction process renders valuable matter, see fig. 5.

CHEMICAL CONVERSION

The most important one of the nitrated aromates is 2,4,6 trinitrotoluene, generally known as TNT. TNT, for its reactive nitric families, is especially suited for a chemical conversion. To eliminate the explosive characteristics from this compound, the NO_2 -families have to be removed or converted. This is best achieved with catalytic reduction which employs hydrogen, H_2 . The resulting 2,4,6 triaminotoluene (TAT) has no explosive character. Reaction is achieved with 98% efficiency and was first carried out by Hein and Wagner in form of a lab-scale test [1]. In the 70ies, BASF tried to manufacture isocyanates to serve as educts (basic material) of polyurethane [2, 3]. From 1990 on, the armament industry (Rheinmetall and Dasa) installed pilot plants to hydrogenate TNT [4, 5].

Hydrogenation of TNT leads to 2,4,6 triaminotoluene in a first step. Using NaBH_4 and applying tough conditions like high temperature and pressure, it is possible to hydrogenate the aromatic ring to methyl 2,4,6 triaminocyclohexane (fig. 6, 7).

Hydrogenation of TNT is achieved in polar solutions with intensive stirring and adding a catalyst under simultaneous introduction of hydrogen. Reaction can be observed with ^1H -NMR and IR spectroscopy or with thin layer chromatography. Hydrogenation is achieved in several steps (fig. 4), reaction velocity being a function of temperature and catalyst to a large extent. Low temperatures are sufficient to obtain reaction. The hydrogen consumption at 25 to 35°C is very high, at 60°C the reaction velocity and the desorption of hydrogen are competing (fig. 8). We tried four types of catalysts and found out, that the best was palladium (fig. 9).

With 2% palladium catalyst relative to the TNT mass, reaction can no longer be controlled. The strongly exothermic reaction ($\Delta H = -1850\text{kJ} \cdot \text{mol}^{-1} \text{ TNT} = -8145\text{kJ} \cdot \text{kg}^{-1} \text{ TNT}$) requires small reactor volumina and large heat exchange surfaces for cooling (fig. 10) [6,7].

The influence of the solvent is shown in fig. 11. The consumption of hydrogen is used as a measurement unit for the reaction velocity. Over a wide range, the reaction velocity is proportional to the amount of catalyst (fig. 12). To control the reaction, defined temperatures and low percentages of catalyst are advisable (fig. 13).

A continuous installation for the hydrogenation of TNT is shown here. There, TNT is dissolved in relatively small amounts. In a solution of 5 - 10% there is no danger of detonation or deflagration. Such solutions are not detonable (fig. 14).

Hydrogenation of the benzole core of 2,4,6 Triaminotoluene or TNT is achieved with the conversion of NaBH_4 (fig. 15) [8,9]. This creates Methyltriaminocyclohexane (MeTACH) which can be available in 8 potential stereoisomeres (fig. 15 shows only one stereoisomere).

The use of NaBH_4 to achieve core hydrogenation, however, proves to be very expensive. Trials to transfer TNT with hydrogen in the presence of catalysts directly into methyltriaminocyclohexane supplied only unsatisfactory yield [8].

TAT is very reactive and not stable at higher humidity (fig. 16). Interesting possibilities of synthesis which would be at hand are the conversion of 2,4,6 Triaminotoluene with phosgen (COCl_2) into 2,4,6 Toluenetriisocyanate (TICT) [10] or hydrolysis into 2,4,6 Trihydroxytoluene (THT) (fig. 17).

Tri-isocyanates can be used to serve as an additive for di-isocyanates like hexamethylene di-isocyanate used in polyurethane formulations by the industry, with which the properties of plastics could be influenced, as tri-isocyanates lead to tridimensional polymerisation (fig. 18).

As core-hydrogenated iso-cyanates are considerably less sensitive against UV radiation than aromatic isocyanates (the secondary chain is stabilised against attack by radicals), a simple catalytic hydrogenation of TNT into methyltriaminocyclohexane is desirable [11].

Presentation of 1,3,5 trihydroxybenzole (phloroglucinol) obtained from 2,4,6 trinitrobenzole (TNB) is achieved in the same way as the synthesis of 2,4,6 tri-hydroxytolouene (fig. 19).

Another example for the chemical conversion of high explosives is hydrolysis of glycerine-trinitrate. Hydrolysis however, produces useful matter only with nitrates. Nitramines like hexogen are decomposed into formaldehyd and ammonia with this type of conversion [12], fig. 20, 21.

Commercial Aspects of Chemical Conversion

The products obtained from the chemical conversion of high explosives are all classical chemical basic materials which are already produced in large quantities. The market possibilities are correspondingly unfavourable. This applies most of all for 2,4,6 toluene triisocyanate, cellulose, glycerine, pentaerythrite and ammonium nitrate.

Phloroglucinol (see above paragraph) serves as a synthesis element in the pharma industry and moreover as an additive for cosmetics and photo developers. The price for phloroglucine is about 180 to 220 DM per kg. A new way of synthesis would be interesting for this valuable product. As, however, the worldwide need in phloroglucine is about 150 to 200 annual tons, provision of 15 to 20 million DM investment funds required for the establishment of a plant to manufacture phloroglucine from tri-nitrobenzole is uninteresting [13] (fig. 22).

The development of a chemical process using high explosives as raw materials needs time and experience in high explosives and their chemical processing. The estimated time schedule is given here (fig. 23).

Biological Decomposition of High Explosives

Decomposition of high explosives using bacteria would be imaginable. However, the problem is the low solubility of the high explosives in water which represents the medium which the bacteria need. To be able to dissolve TNT, the solubility in water of which is about $0,5 \text{ mmol} \cdot \text{l}^{-1}$, in a measurable time, feeding of 20mmol glucose and ammoniumsulfate each is necessary. TNT up to $50 \text{ mmol} \cdot \text{l}^{-1}$ is soluble in alcohol water solutions (fig. 24).

The low solubility, temperature stabilisation of the solution to 35 - 40°C and adding of glucose, ethanole and other nitrogenous or carbonic nutriments needed by the bacteria cause enormous expenditure of funds so that a large-scale plant for the biological decomposition of high explosives appears impossible. The biological conversion of TNT works only if the process is split up into two different processes, an anaerobic and an aerobic process with two different types of bacteria and process parameters (fig. 25).

This is still completed by the fact that about one third of the formulation is reduced only partially [14]. The metabolites which still contain nitrogen families are by far more poisonous than TNT. Other explosives like HMX and RDX are hardly processible because they are nearly insoluble in water [14].

Another disadvantage is the fact that high explosives are available as mixtures (compounds) in most cases so that intensive processing and chemical pre-treatment is necessary, to have the substances ready for biological decomposition [15].

A normal double base propellant contains lead and copper salts which are highly toxic to all bacteria. A separation of these materials is feasible but not payable (fig. 26).

The problems of the biological treatment of H.E. are the low solubility in water, the high energy and nutrition consumption, the sensitivity of the bacteria to metal salts and the incomplete degradation of the high explosives with the formation of very toxic metabolites (fig. 27).

High Explosive Recycling

Military high explosives are normally crystalline organic compounds, which can be recrystallised. Recycling, i.e. cleaning and recovery of high explosives like TNT, HMX, RDX in principle, is possible, but the value of these substances has to be considered. One kilogram TNT for civil or military purposes is available on the world's markets for 1 to 5 DM, according to quality, RDX for about 25 to 30 DM and HMX for about 60 to 80 DM. Thus, recycling appears interesting only for HMX, as large quantities of solvents and suitable facilities are required for the processing of high explosives that have to be subjected to the relevant approval and authorisation procedures. Recovered high explosives have to be re-qualified for military or commercial use, which means that they have to pass a comprehensive acceptance test procedure (fig. 28).

Use in Civil High Explosives

It was often suggested to crush military H.E. charges and to add the residues to civil high explosives. The problem which occurred there was manifested by the different character of regulations and requirements that apply for military and civil high explosive charges and their various qualification methods.

TNT for example presents a very negative oxygen balance (-74%) which permits adding of TNT only in smallest quantities for mining purposes. The CO percentage admissible after firing is extremely restricted because of the risk of firedamp [16]. Adding it to H.E. charges used in openpit mining is in principle, possible.

Military high explosives, however, prove to be extremely detonable and therefore they can be admixed to slurry explosive charges only in small quantities as the grain size distribution of the fired matter undergoes considerable changes.

Slurry explosive charges are compounds that can be transferred in pumps and consist of oxidation substances - in most cases ammonium nitrate, water and fuels that are used exclusively for civil purposes. It is most of all due to the applicable extensive safety approvals that only extremely small amounts of military high explosives could be processed in civil high explosive charges.

Thermal Disposal of High Explosives

Uncontrolled burning of propellants and explosives pollutes the air with various gases like NH_3 , HCN and NO and produces also a lot of soot which is charged with condensed, highly toxic aromatic compounds (fig. 30, 31).

Controlled combustion of high explosives offers a series of advantages. Also compounds which are hardly separable can be burned. The energy contents of high explosives are in most cases overestimated. The table contains a comparison of the calorific value of high explosives and that of normal fuels (fig. 32). To reach the temperatures that are required for complete combustion, it is necessary to feed external energy.

This represents controlled burning in a rotary kiln with subsequent flue gas purification (fig. 33) which leads to high investment and maintenance cost due to the applicable safety and environment regulations that have to be observed. A high explosive combustion plant is running smoothly in Saxony / Germany since mid of 1994 [17].

Outlook and Assessment of Processes

Considering the individual processes applied for the conversion of high explosives results in a variety of technical and commercial aspects. Recycling in form of re-use is attributed very high importance by the society but has to remain affordable. This means that its application on cheap and dangerous products it is uninteresting, while it is considered for expensive high explosives like RDX.

Chemists' dreams of syntheses using annuated high explosives as educts fail because of the immense investments required to build facilities for the conversion of these substances and the utmost abundant variety of products found on the world's markets.

At first sight, the biological decomposition of high explosives appears to be a promising idea. It is, however, very expensive as it has to be based on pure substances and leads to product compounds that can hardly be separated.

An affordable way to annihilate high explosives extracted from annuated ordnance which can be achieved at short notice, is burning. The example "conversion of high explosives" shows that the desirable protection of the environment and preservation of resources is not always economically interesting and thus, feasible (fig. 34, 35).

List of Terms

Propellants consist of different high explosives and are sub-divided into:

Single base propellants which consist of mere cellulose nitrates (nitrocellulose) and a radical catcher to achieve aging protection.

Typical composition:

98% Nitrocellulose with varying nitrification degrees (11.6 - 13.3%).
2 % Diphenylamine as radical catchers for NO₂ radicals.

Main use: propellant for small calibered munition.

Double base propellants

The two high explosives cellulose nitrate (nitrocellulose) and glycerine nitrate (nitroglycerine) serve as energy carriers.

Typical composition:

50% Nitrocellulose
40% Nitroglycerine
1 % Copper salicylate (combustion moderator)
2,5 % Lead resorcinate (combustion moderator)
2 % 2,4 di-nitrodiphenlyamine (radical catcher)
4 % Di-n-propyladipate (additive)
0,5% Potassium kryolithe K3AlF6 (flame suppression)

Main purpose of use: rocket motors for military purposes.

Triple base propellants:

Three energy carriers define the formulation.

Typical composition:

50% Nitrocellulose
20% Nitroglycerine
20% Nitroguanidine
2% Akardite (di-phanylmethyl urea)
0,5% Potassium kryolithe (K3AlF6)

Main purpose of use: propellant for big calibered munition.

Composite propellants:

Contrary to the homogeneous single, double and triple base propellants, composite propellants are regarded heterogeneous. They consist of an oxidation agent, anorganic salt and a plastic component - in most cases this is a polyurethane which acts simultaneously as binding agent and as fuel. In many cases, ferrous oxides are used to serve as a combustion moderator.

Typical composition:

85% Ammonium perchlorate
 13% Polyurethane / hydroxy terminated polybutadiene and isophorone di-isocyanate
 2% Ferrous (III) oxide

Main purpose of use: military and civil long range rocket motors (e.g. space shuttle propulsion).

Oxygen balance:

This represents the percentage in oxygen (in percent by weight) available during detonation which means conversion into H_2O , CO_2 , NO_2 , Al_2O_3 etc. As soon as the percentage in oxygen bound in the high explosive is insufficient to ensure a complete conversion this is regarded a negative oxygen balance; as soon as the percentage in oxygen is sufficient or presents a surplus, this is regarded a positive oxygen balance.

Examples:

TNT ($C_7H_5O_6N_3$)	-74,0 %
Nitroglycerine ($C_3H_5O_9N_3$)	+ 3,5 %
Ammoniumnitrate (NH_4NO_3)	+ 20,0%

Conversion of High Explosives

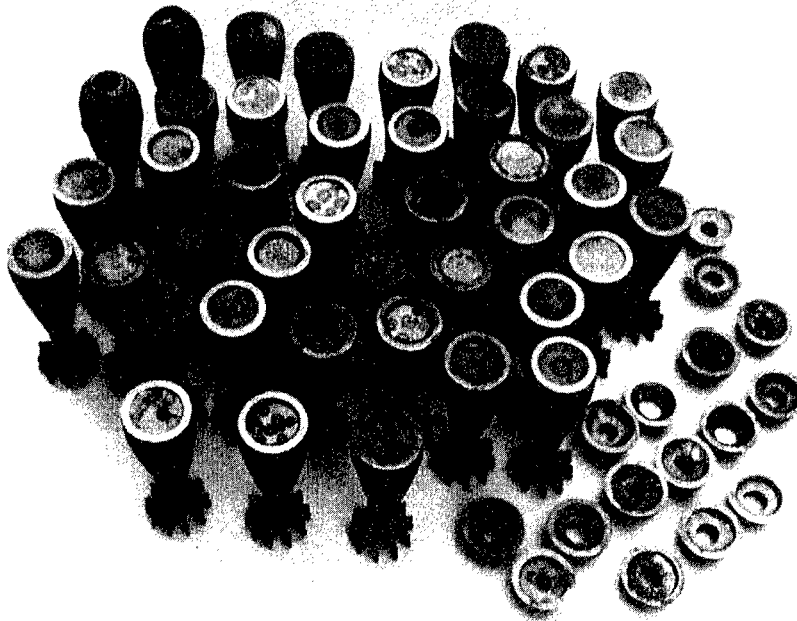
—— Dreams and Reality ——

Dr. P. Wanninger

**Rheinmetall
W&M GmbH
Unterlüß**

- **Chemical Conversion**
 - **Commercial Aspects of Chemical Conversion**
 - **Biological Decomposition of High Explosives**
 - **High Explosive Recycling**
 - **Use of Civil High Explosives**
 - **Thermal Disposal of High Explosives**
 - **Outlook and Assessment of Processes**
-

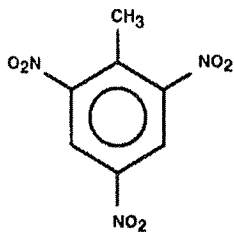
Water jet cut ammunition



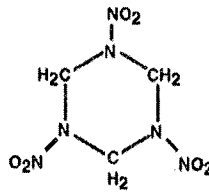
Formulations of Ammunitions

HE Charges	TNT	RDX	HMX	Binder				
	15 - 35	65 - 85						
	15 - 25		75 - 85					
		95		5				
			95	5				
Propellants								
Single base	NC	Stabilizer	Graphite					
	97,5	2	0,5					
Double base	AP	NC	NG	AI	Stabilizer	Burning modifiers	Plasticizer	Binder
	0 - 20	45 - 50	30 - 40	0 - 15	1 - 2	3 - 5	5 - 10	
Composite	80 - 85			0 - 20		2 - 4	2 - 5	15 - 20

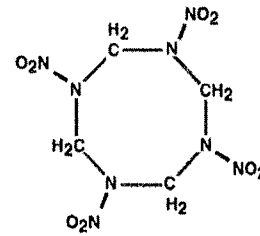
Explosives



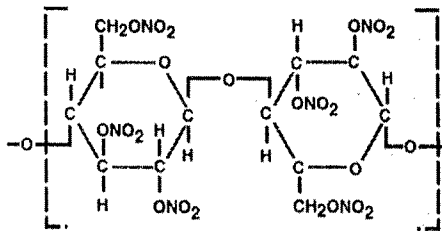
2, 4, 6 - Trinitrotoluol
TNT



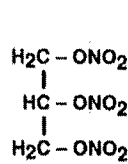
Cyclo 1, 3, 5
Trimethylen 2, 4, 6 - Trinitramin
Hexogen, RDX



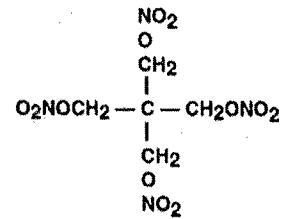
Cyclo 1, 3, 5, 7 - Tetramethylen
2, 4, 6, 8 - Tetranitramin
Oktogen, HMX



Cellulosenitrate, Nitrocellulose
NC

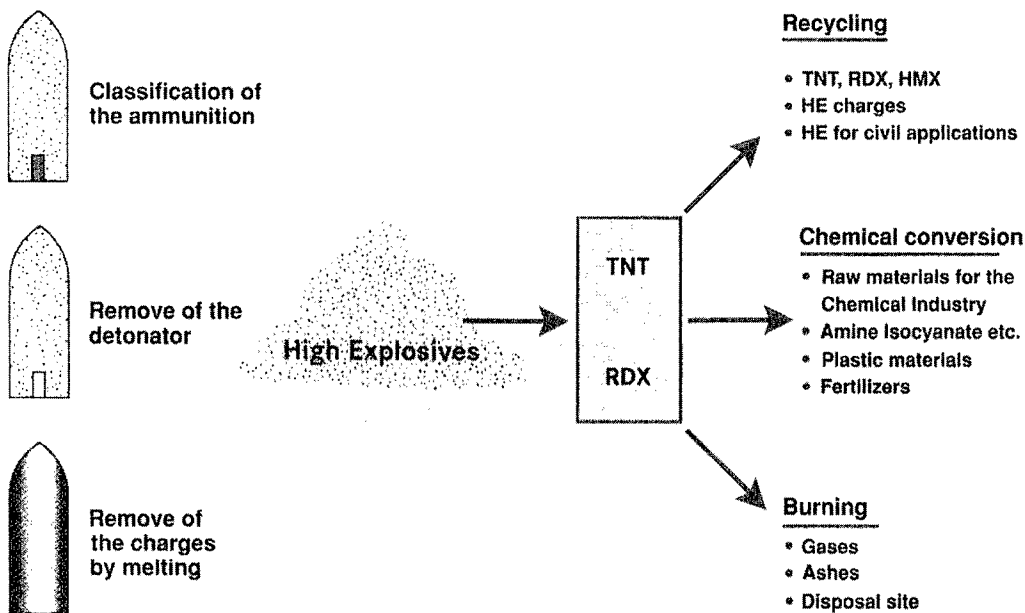


Glycerintrinitrate
Nitroglycerin
NG



Pentaerythritetranitrate
Nitropenta
PETN

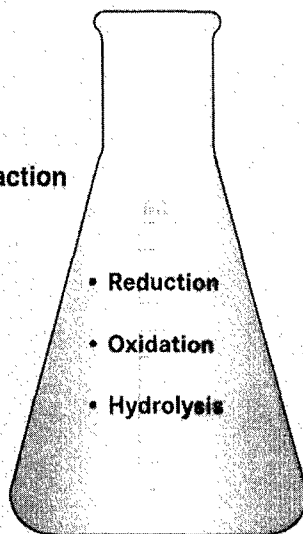
Demilitarisation



Chemical Conversion of Explosives



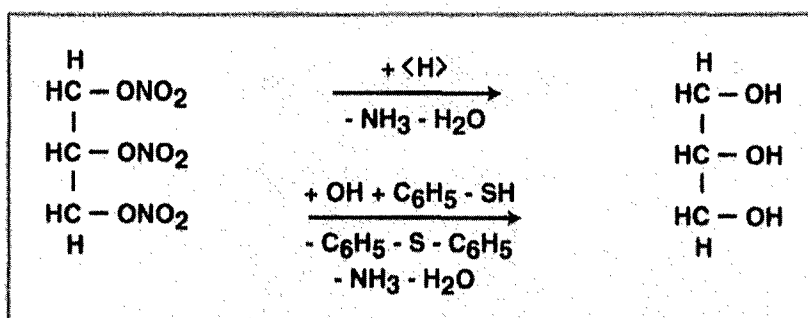
Reaction



Chemical Conversion of Explosives

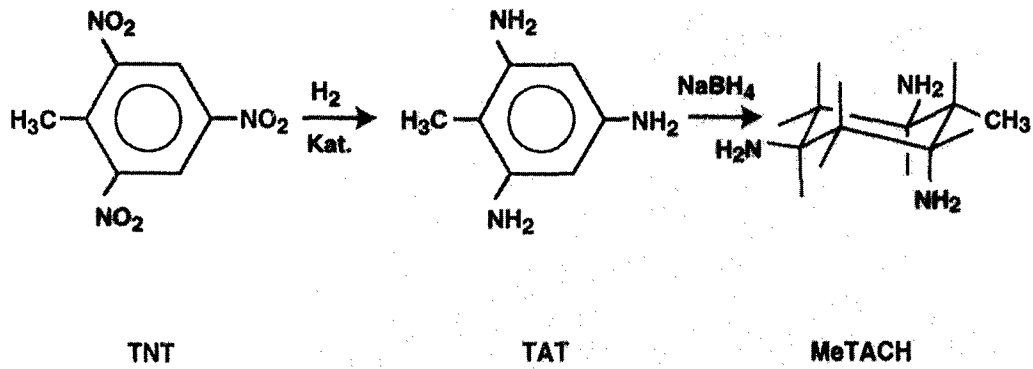


Chemical Inertisation



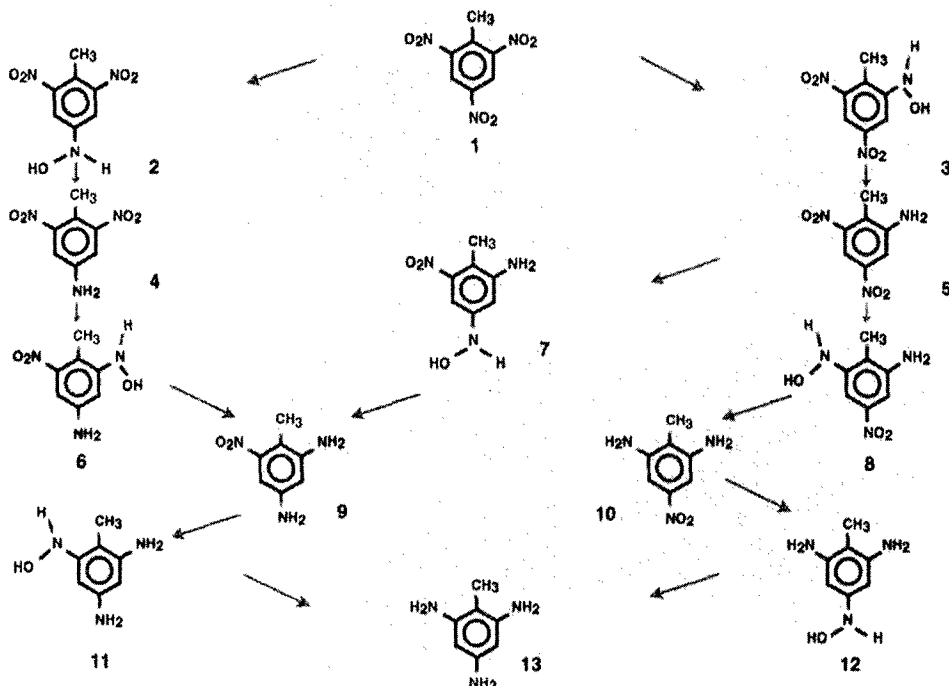
Chemical Conversion of Explosives

Hydrogenation of TNT

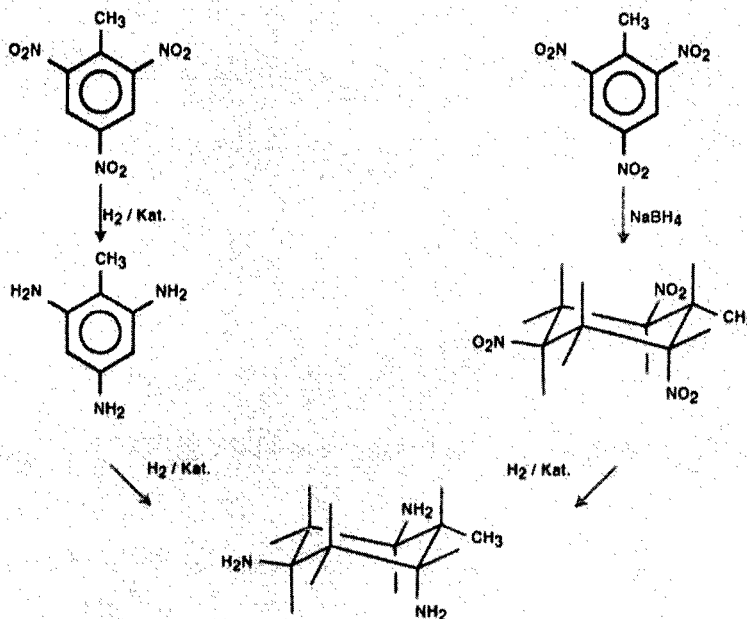


Chemical Conversion of Explosives

Hydrogenation of TNT

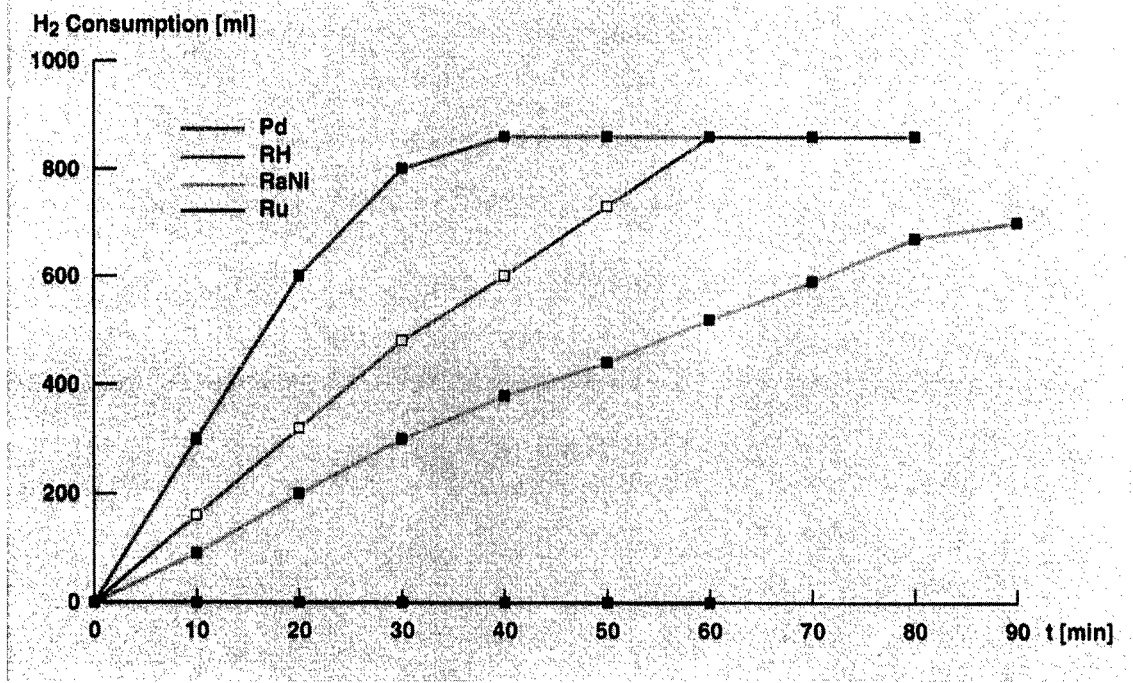


Synthesis of MeTACH



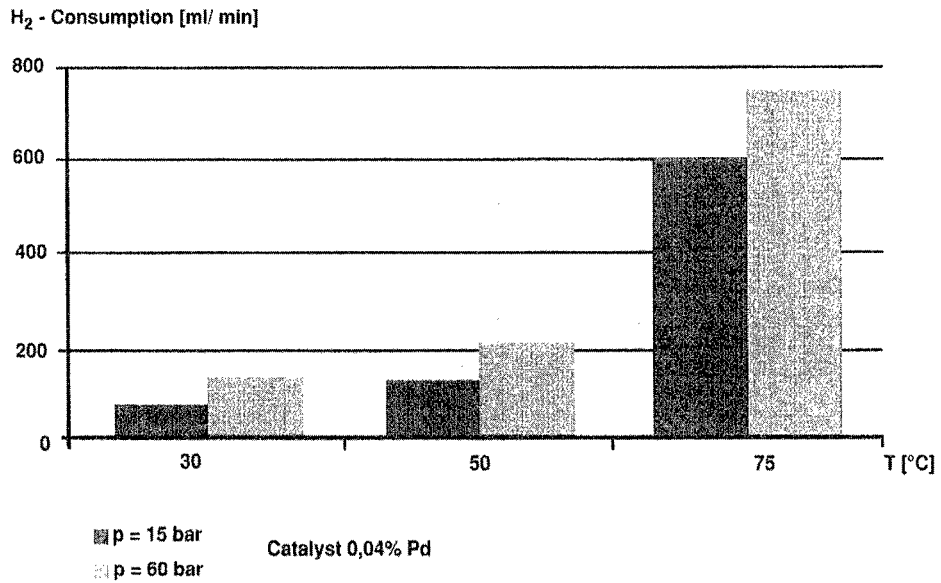
Hydrogenation of TNT

Influence of Catalyst



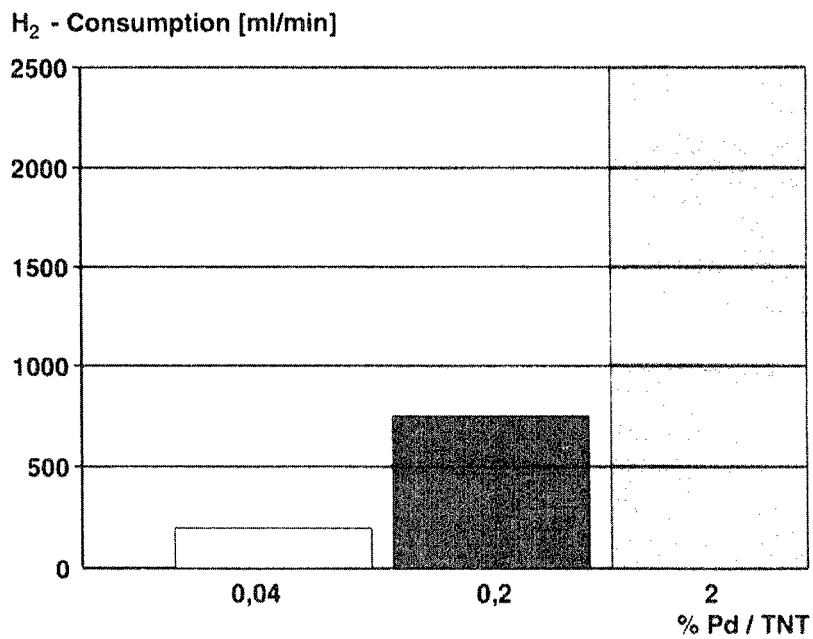
Hydrogenation of TNT

Reaction velocity vs. pressure and temperature



Hydrogenation of TNT

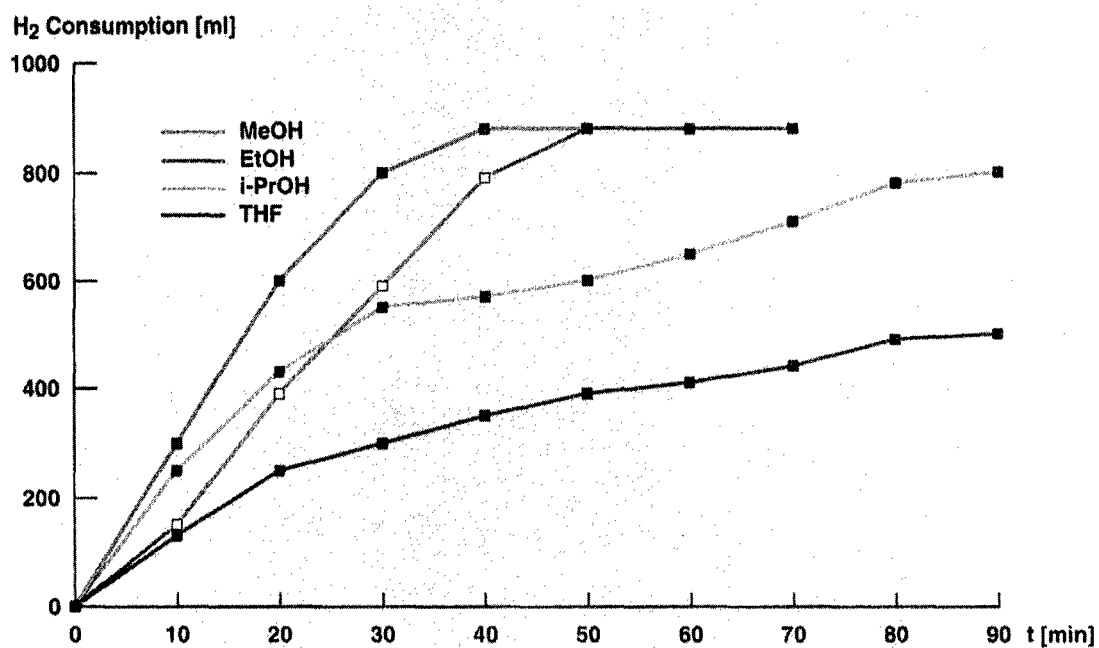
Reaction velocity vs. concentration of catalyst



Hydrogenation of TNT



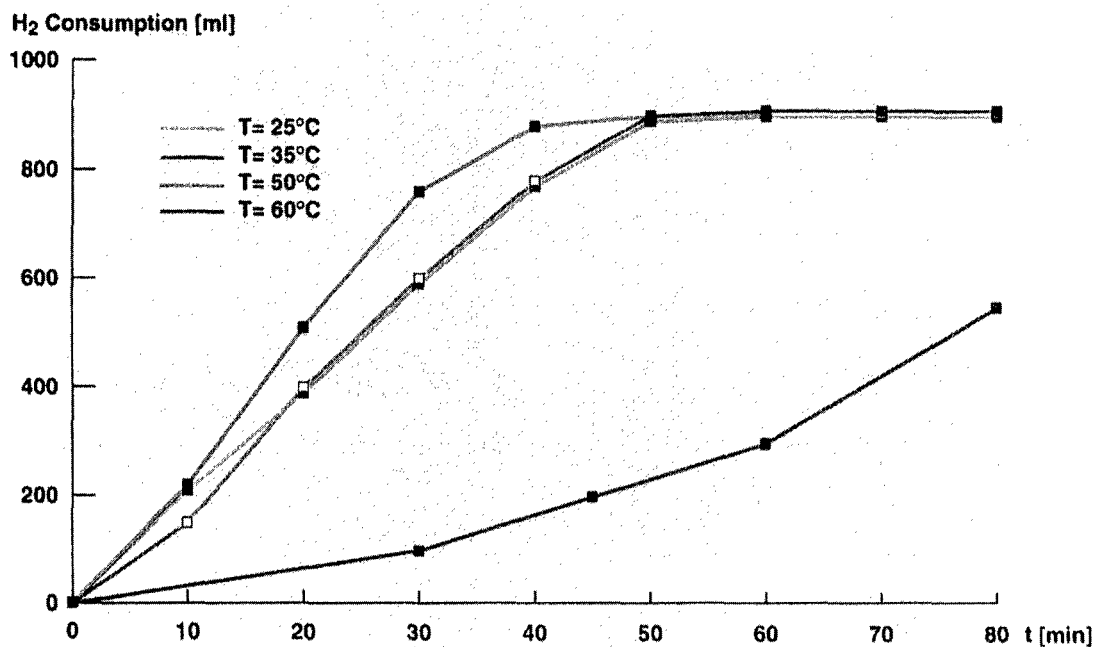
Influence of Solvent



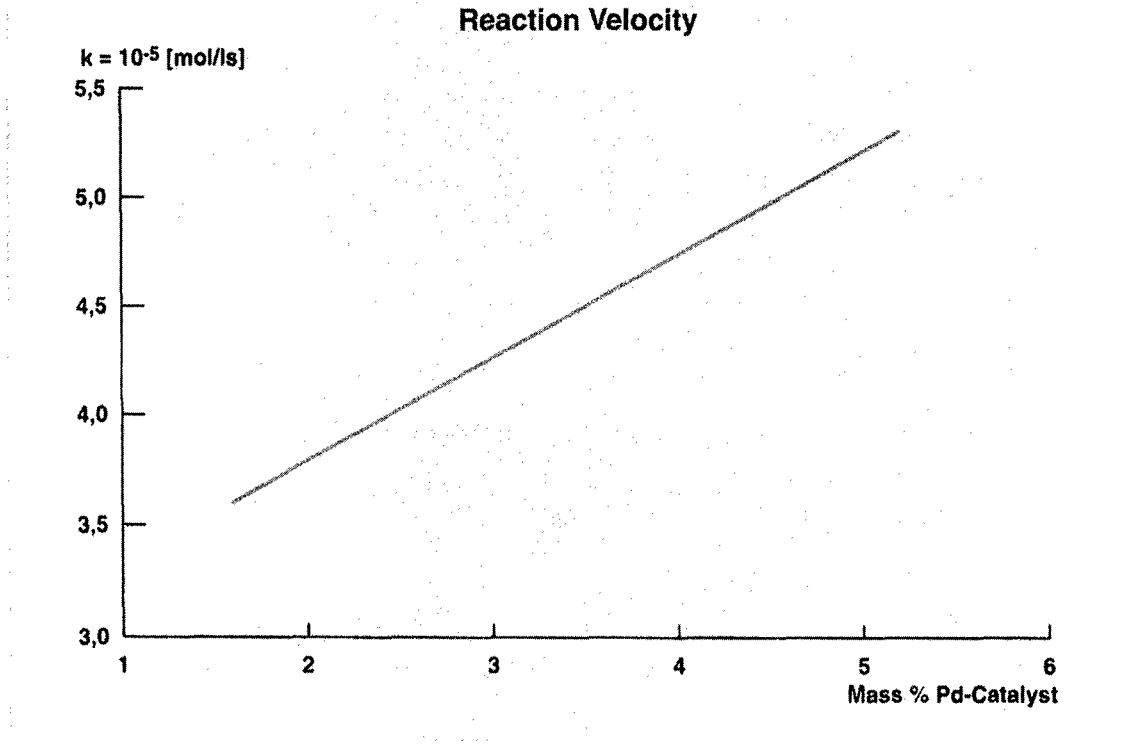
Hydrogenation of TNT



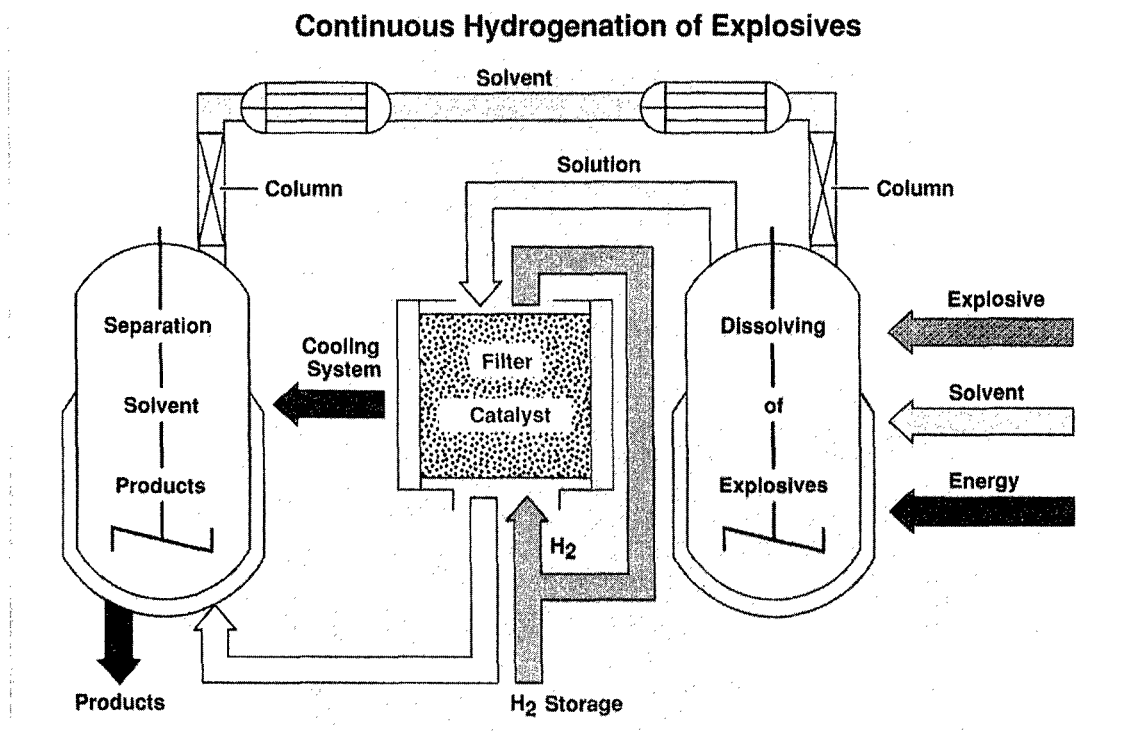
Influence of Temperature



Hydrogenation of TNT



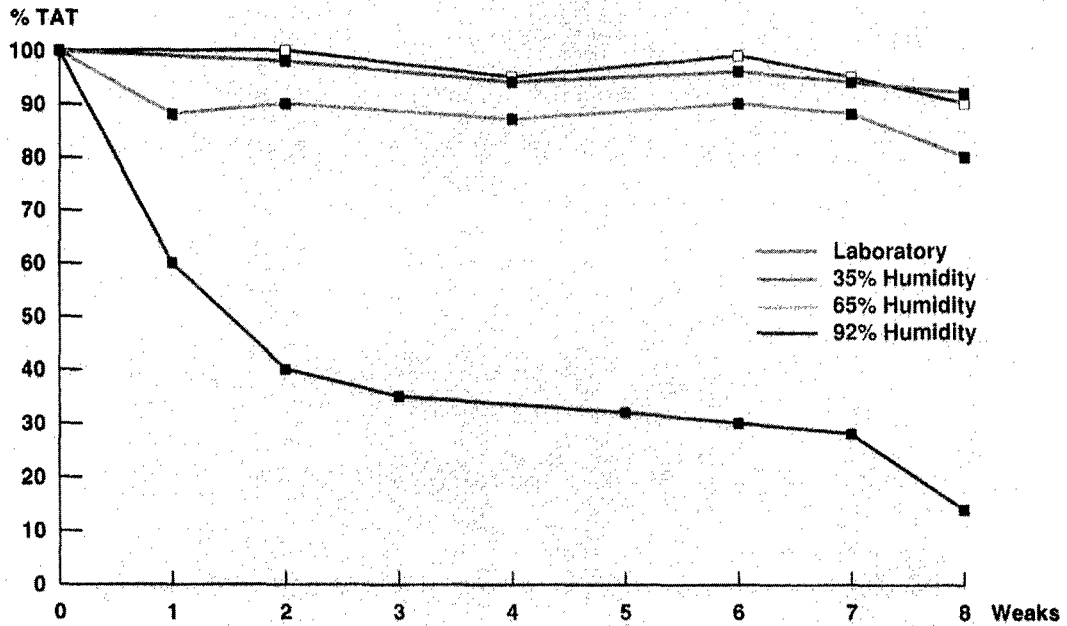
Chemical Conversion of Explosives



Chemical Conversion of Explosives



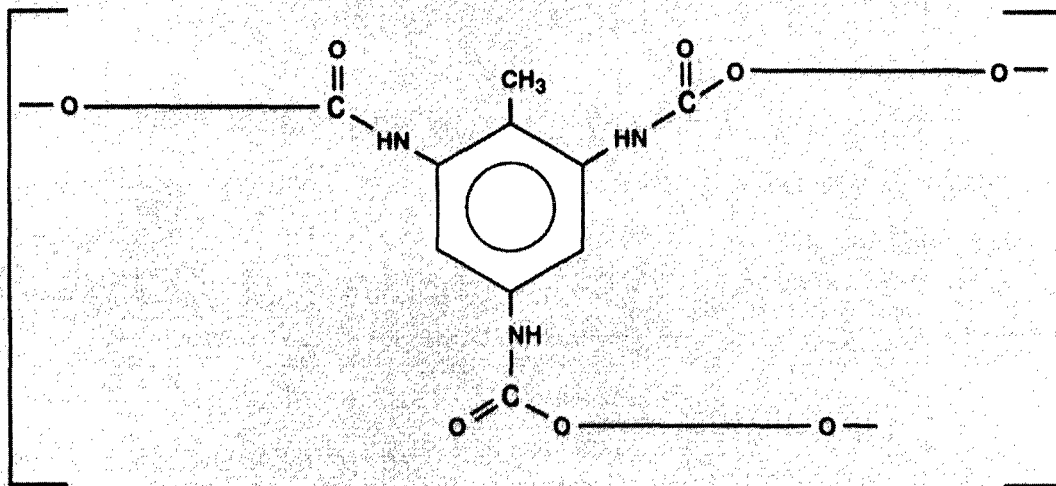
Stability of TAT at defined humidity



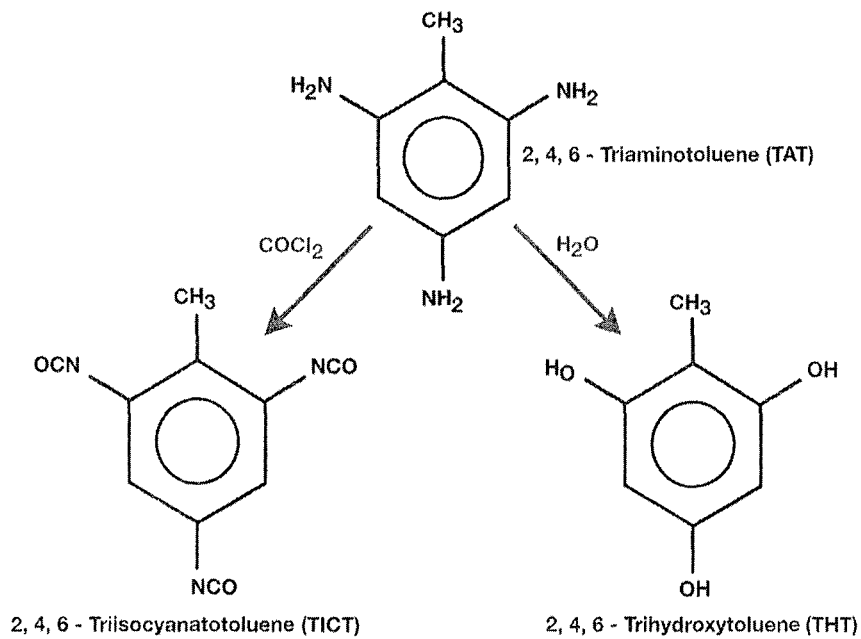
Chemical Conversion of Explosives



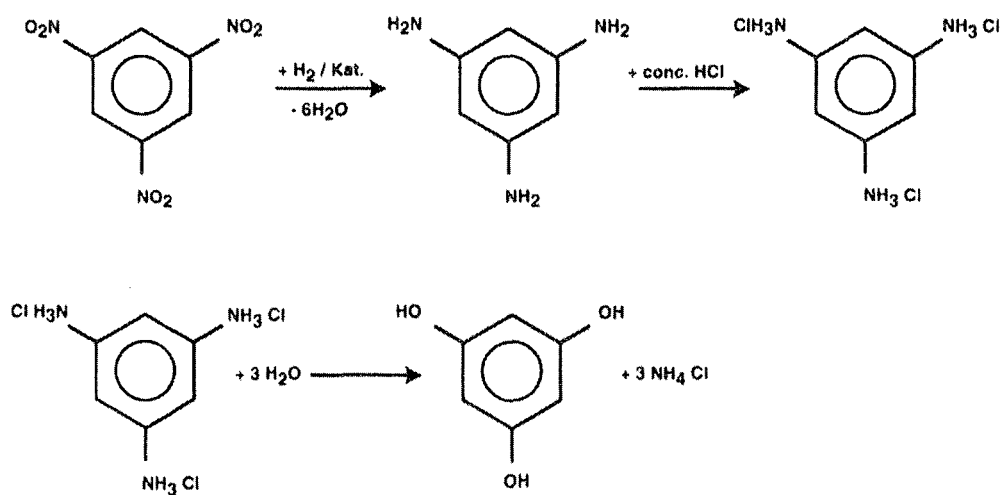
Polyurethane



TAT Reaction Products



Synthesis of Phloroglucinol



Chemical Conversion of Explosives



Use of Products

Raw material	Products	Evaluation
TNT	2, 4, 6- Triaminotoluene TAT 2, 4, 6- Triaminomethyl- cyclohexane, TAMC	Higher value products
RDX HMX	Formaldehyd, Methanol NO _x Nitrogen Ammonium	Waste
NC	Cellulose and Nitrate	Commodities
NG	Glycerine and Nitrate	Commodities
PETN	Pentaerythrite and Nitrate	Commodities
AP (NH ₄ ClO ₄)	NH ₄ Cl	Commodities

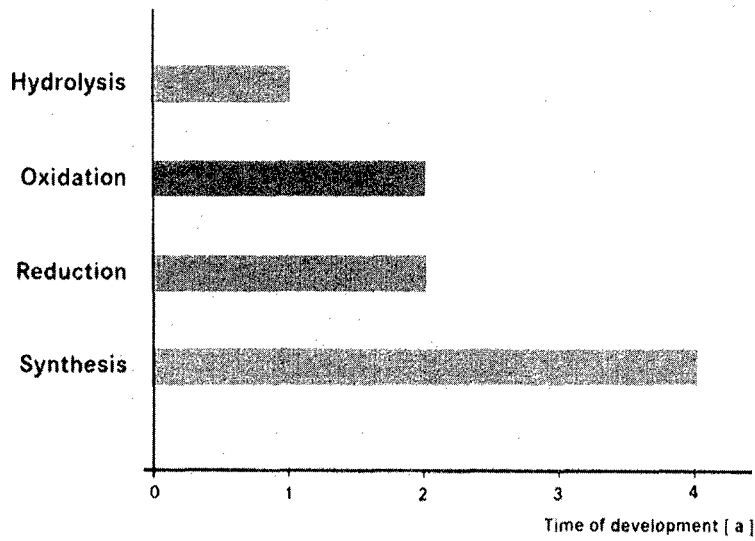
Chemical Conversion of Explosives



Conversion of Explosives

Raw material	Product	Annual production in USA and Western Europe 1990 [10 ³ t]
Dinitrotoluene	Toluenediisocyanate	870
TNT	Toluenetriisocyanate	0
NC	Cellulose	4 400
NG	Glycerine	550
PETN	Pentaerythrite	260
Nitratester	Ammoniumnitrate	14 800
TNB	Phloroglucinol	0,15

Chemical Conversion of Explosives



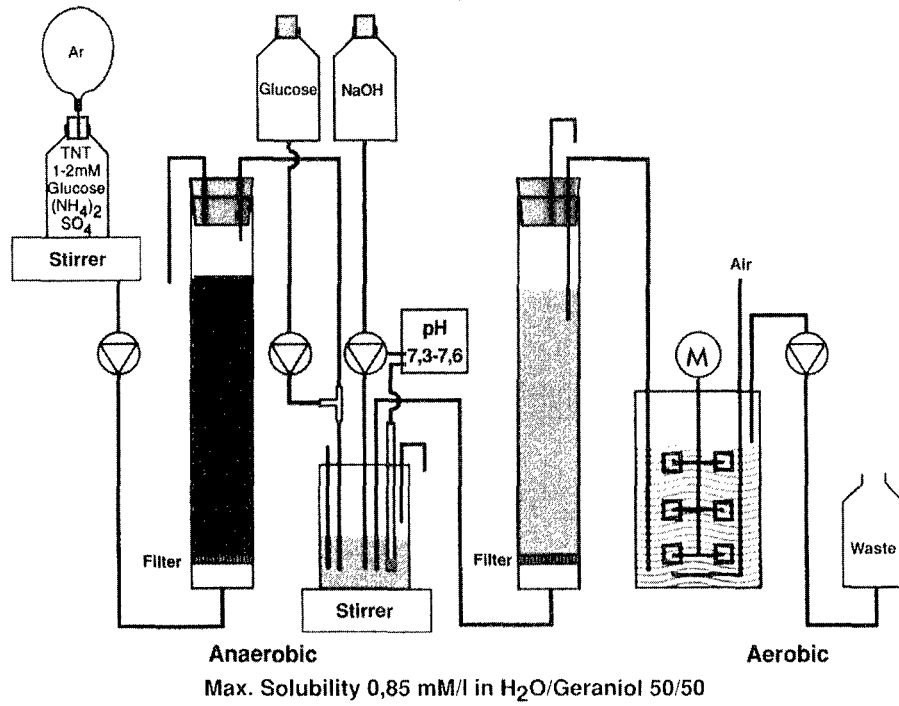
Chemical Inertisation

<u>Advantages</u>	<u>Disadvantages</u>
High explosives are valuable raw materials	
Synthesis of new products	

Biological Conversion of TNT



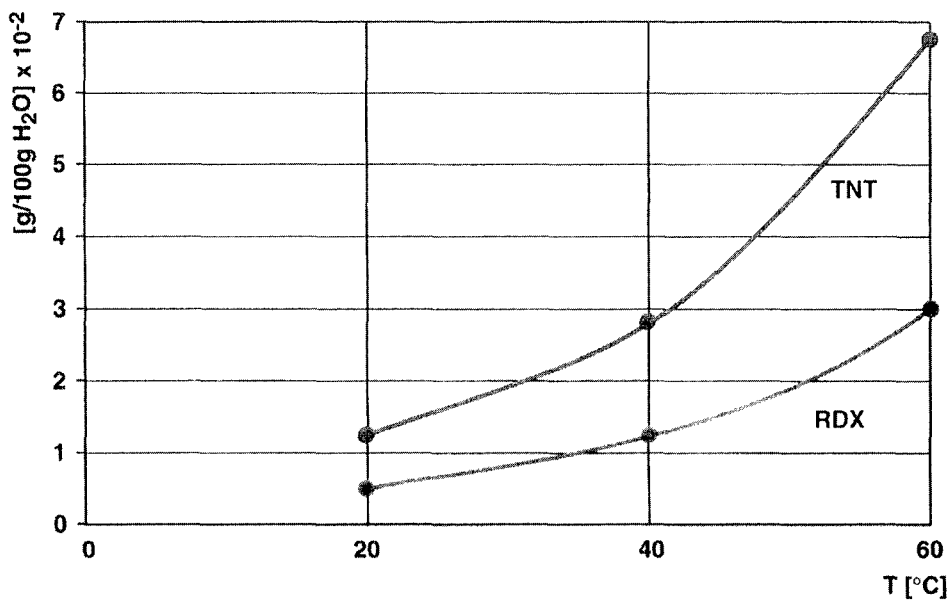
Laboratory Reactor



Biological Conversion of Explosives



Solubility



Double base propellants

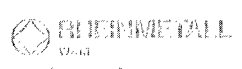
Typical formulation

- 50 % Nitrocellulose
- 40 % Nitroglycerine
- 1 % Copper salicylate (combustion moderator)
- 2,5 % Lead resorcinat (combustion moderator)
- 2 % 2,4 Di-nitrodiphenylamine (radical catcher)
- 4 % Di-n-propyladipate (additive)
- 0,5 % Potassium kryolithe K_3AlF_6 (flame suppression)

Problems

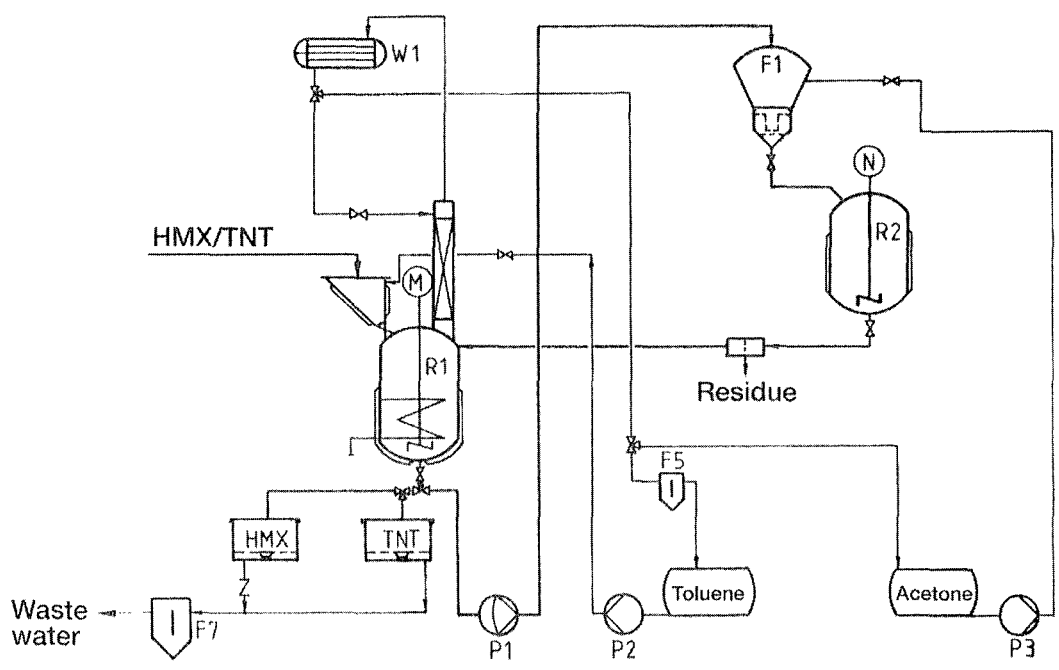
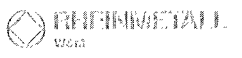
- Solubility in water
 - Big quantities of warm water are necessary
- Big quantities of glucose are necessary
- Toxicity of ingredients (e.g. coppersalts)
- Very toxic metabolites

Biological Incineration



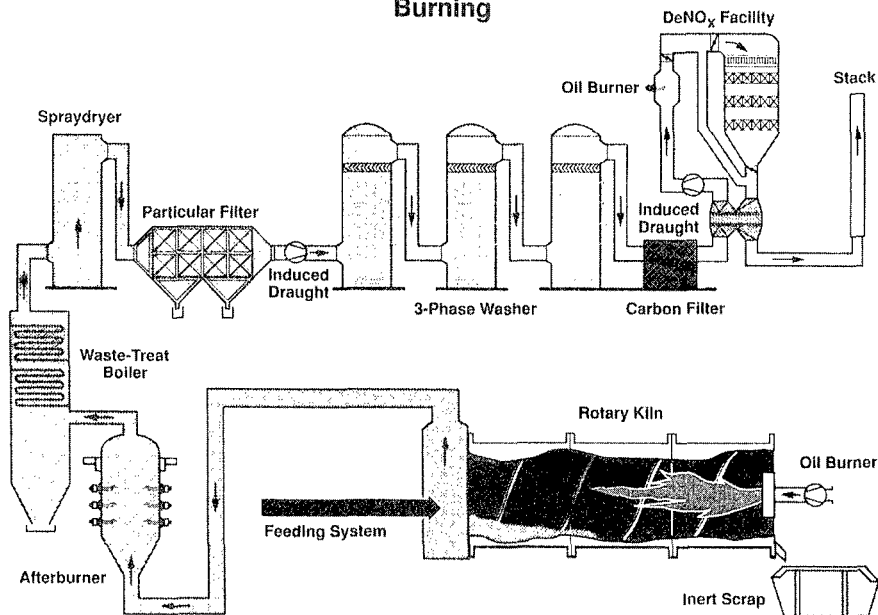
<u>Advantages</u>	<u>Disadvantages</u>
High public Acceptance	Mostly pure raw materials required
For contaminated soil	Chemical steps
For waste water	Minimum solubility required
	High energy consumption
	Longtime duration
	Yield
	Cost

HMX-recycling



<u>Advantages</u>	<u>Disadvantages</u>
Environment protection	Big Invest necessary
Save energy	New qualification required
Save solvents etc.	Stock of raw materials necessary
Influence on quality of the product	High purity of raw materials required
Cost	

Disposal of Explosives Burning



Oxygen Balance



Nitrocellulose	-28,6 %
Tetryl	-47,4 %
RDX	-21,6 %
HMX	-21,6 %
TNT	-74,0 %

Thermal Decomposition of Explosives



Combustion Enthalpy [kJ/kg]

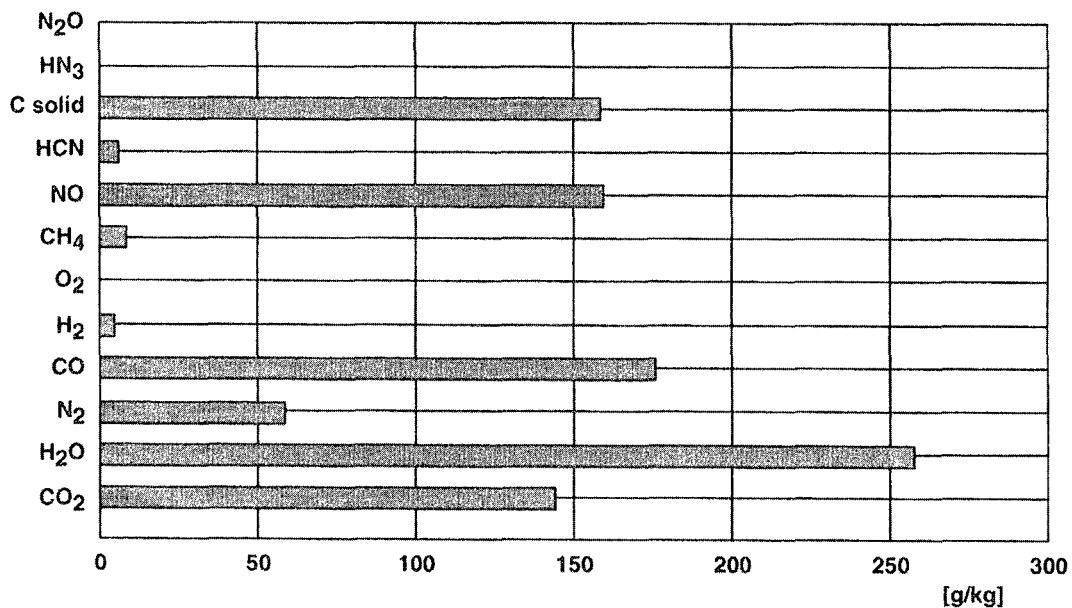
Explosives		Fuels	
TNT	15 146	Wood	15 700
RDX	9 560	Charcoal	31 000
HMX	9 883	Gasoil	43 960
NC	9 677	Ethylene	50 790
NG	6 761	Ammonia	22 360

Explosivstoffentsorgung Entwicklung der Genehmigungswerte

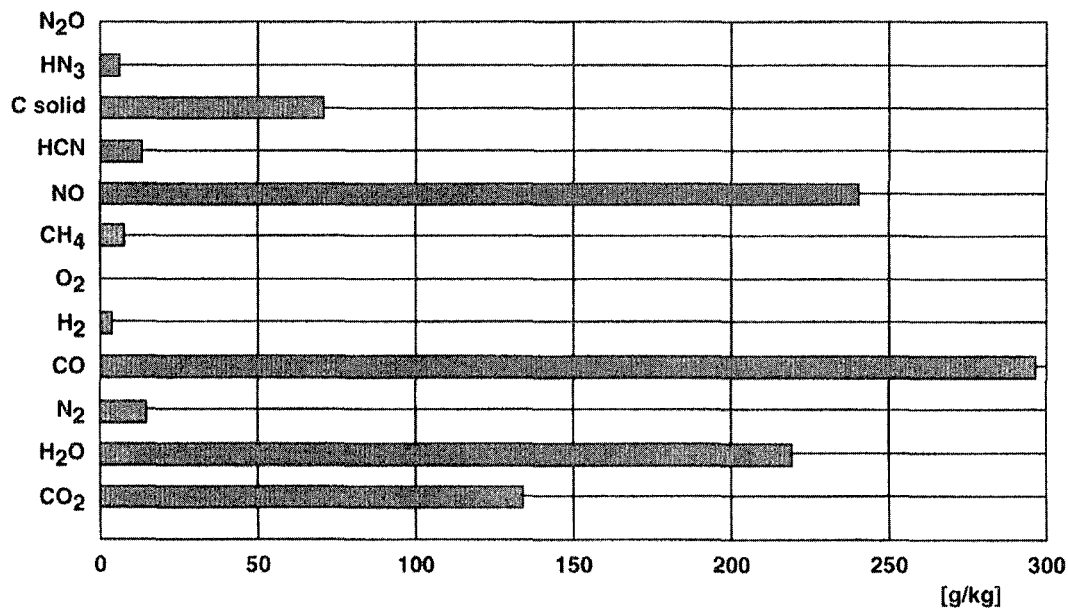
Stoffart	TA Luft 1974	TA Luft 1986	Grenzwerte für neue Genehmigungen
HCl	100 mg/cbm i.N.	50 mg/cbm i.N.	5 - 30 mg/cbm
(NO) _x	---	500 mg/cbm i.N.	300 mg/cbm
CO	1000 mg/cbm i.N.	100 mg/cbm i.N.	100 mg/cbm
Staub	100 mg/cbm i.N.	30 mg/cbm i.N.	10 - 30 mg/cbm

Thermal Decomposition

Gases of burned single base propellants



Gases of burned double base propellants



<u>Advantages</u>	<u>Disadvantages</u>
Burning of unknown	Oxygen balance
Mixtures possible	Safety aspects
Less wastes	Pollution
High explosives are totally destroyed	Big investment

Disposal of Explosives



Evaluation of different processes

Material	Recycling	Chemical Conversion	Biological Degradation	Burning
HE charges				
TNT	+↓	+↑	+↓	+↑
RDX	+↓	0↓	0↓	+↑
HMX	+↑	0↓	-	+↓
Propellants				
NC	-	0↓	+↓	+↑
NG	+↓	0↓	0↓	+↑
AP	+↑	0↓	-	+↑

- + large scale production possible
- 0 feasible
- not feasible
- ↑ useful business management
- ↓ not useful business management

Disposal of Explosives



Evaluation of different processes

Material	Recycling	Chemical Conversion	Biological Degradation	Burning
HE charges				
TNT / RDX	+↓	+↓	0↓	+↑
TNT / HMX	+↑	+↑	-	+↑
Propellants				
Single base	0↓	0↓	0↓	+↑
Double base	-	0↓	-	+↑
Composite	+↓	0↓	-	+↑

- + large scale production possible
- 0 feasible
- not feasible
- ↑ useful business management
- ↓ not useful business management