

High Energy Compounds – Explosives

***By Professor Dr.Dr.h.c. Randolph Riemschneider
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*Life BWW Fellow Prof R.Riemschneider reports about his early research concerning "Warfare agent compounds" compiling them in the Formula Summaries A-J and tables (1,2).
The editor*

In times of war, the term "explosives" meant death and destruction for millions, but explosives helped the author to survive World War II unscathed. "One person's owl is the other's nightingale" („Wat den een sin Uhl is den annern sin Nachtigall“) was a saying of the author's grandfather who spoke the Low German dialect of the Lüneburg district. This referred to the author's research at the "OKH (German) Army Research Establishment for Warfare and Explosives" in Prague - far away from the front at the time, in the lion's den, so to speak. This work also gave him the opportunity to conduct chemical experiments - another way of "survival by research"; cf. SPECIAL PART A.

**I
in Berlin, 1942**

On the occasion of the author's presentation and visit at the OKH (Oberkommando des Heeres: German Army High Command) in Berlin Jebenstrasse im Winter 1942 he held several lectures, two in the conference hall and a third one before the interview, entitled:

- "Chemical warfare agents" – SPECIAL PART B (3),**
 - "Chemical propellants for rockets" - SPECIAL PART C (4),**
 - "N-rich high energy compounds" – *Formula Summaries A-J* (1,2)**
- to demonstrate his qualification and knowledge in this line of chemistry.**

These lectures were chaired by Major Kassuba who gave each time the introductory address - as well some days later leading the real presentation interview. For the interview and discussion the author had prepared some plates, three of them reproduced here as *Plate 1a*, *1b*, *2*, and *3*. After the interview the author handed over to Major Kassuba some documents listed in SPECIAL PART D.

With *Plate 1a* and *1b* the author continued and completed his last lecture given some days before. On basis of *Plate 2* the author informed about his earlier corresponding experiments that could be continued if wanted and if time. In *Plate 3* the author showed forward-looking projects.

Plate 1a: N-rich high energy compounds

Plate 1b: *Formula Summary A*

Plate 2: Earlier experiments carried out from the author – interesting in connection with warfare

Plate 3: Projects in future.

Plate 1a: N-rich high energy compounds*

Substitution products of tetrazole (I)	CHN_4R_2
substitution products of triazole (II)	$\text{CH}_2\text{N}_3\text{R}_1$
substitutions products of pentazole (III)	N_5R_1
5-amino-tetrazole (IV) (and salts)	CH_3N_5
1,5-diamino-tetrazole (V)**	CH_4N_6
5-nitrimino-tetrazole (VI)	$\text{CH}_2\text{O}_2\text{N}_6$
1-methyl-5-methylamino-tetrazole (VII)	$\text{C}_3\text{H}_7\text{N}_5$
1,6-dimethyl-6-nitro-tetrazole (VIII)	$\text{C}_3\text{H}_6\text{O}_2\text{N}_6$
salts of azotetrazolat (IX)	$\text{C}_2\text{N}_{10}^{--}$
dinitrobiuret (X)	$\text{C}_2\text{H}_3\text{O}_6\text{N}_5$
diaminodinitroethylene (XI)	$\text{C}_2\text{H}_4\text{O}_4\text{N}_4$
IV-salts e.g. IV-perchlorates, IV-azides, IX-salts e.g. Ba-IX, Ag ₂ -IX, IX-[(CH ₃)N-N(CH ₃) ₂] ₂	

* In the original plate 1a, presented at the OKH visit, were lacking the compounds IV-VIII – completed here.

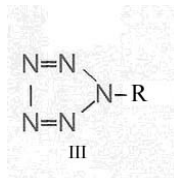
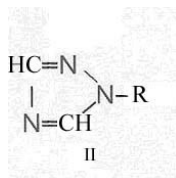
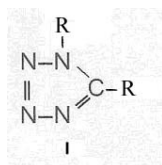
** V has the highest N-content of the tetrazoles and is very stable.

The following *Formula Summaries A - J (Plate 1b,4,5,6 etc)* correspond with Plate 1a etc., also concerning the Roman numbers.

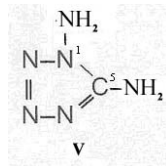
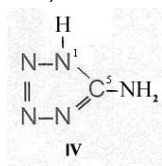
Plate 1b:

Formula Summary A¹

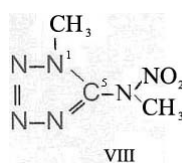
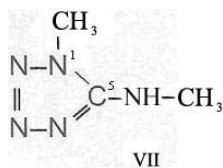
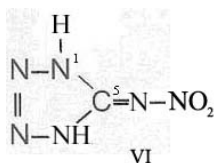
**Projected high-energy compounds of the class of representatives
in N : N₃ to N₁₀ (presented to the OKH in 1942: I-V; IX-XI)²**



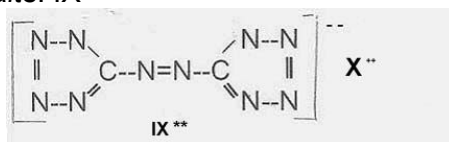
Amino-I derivatives: IV, V



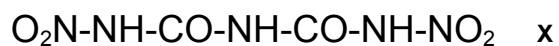
IV- derivatives: VI to VIII



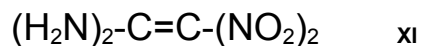
azotetrazolat-salts: IX



biuret-nitration product, i.e.: X



Diamino-dinitro-ethylene: XI



¹ with letter from Dec 12th, 1956 sent to the "Bundesministerium für Verteidigung" in Bonn, confirmed with letter from Dec 21st, 1956; cf Plates F to J and ref (12h)

² starting from J. Thiele, Liebigs Ann.Chem. **270**,1 (1892) and R. Stolle, H. Netz, O. Kramer, S. Rotschild, O. Schick, J. prakt.Chem. **138**, 1 (1933).

**Plate 2: Earlier experiments carried out from the author –
interesting in the connection with warfare**

Nr	Subject	ref
1	Halogen-substitute alkynes (and dienes) ie C_2Cl_2 , C_2HCl (C_5Cl_6)	(5a,b)
2	reactions of acetylen with $ClSF_5$	(6a,b)
3	$ClCH_2SCl$ -chemistry	(7)
4	reaction between CS_2 and $NaCN$	(8)
5	1,2,3-benzotriazole*	(12i,j)

* the author's first example for N-rich high energy compounds [1939 : (12i)]

commentary to Plate 2 (added later):

- to no 1: Manufacturing and new determination of the physical and chemical properties of monofluoroacetylen, monochloroacetylen, dichloroacetylen (5) ; to be tested for explosive propensity and suitability as chemical warfare agents.
 C_2Cl_2 as experiments as rocket fuel
- to no 2: Testing chlorothiopentafluoroethylene, $C_2H_2F_5ClS$, manufactured from acetylene and $ClSF_5$ in 1941 (6a) for suitability as a chemical warfare agent (Jan 43): $HalSF_5 \rightarrow SF_6$ in SPECIAL PART G). This direction of work went back to an initiative by C Weygand, H Kautsky, Leipzig. Further details on $C_2H_2F_5ClS$ and the parent substance obtained from it, acetylenethiopentafluoride, in PROJ XII 4.2 (6b).
- to no 3: Continuation of the work, begun in 1940, in the area of chloromethanethiochloride chemistry (7); cf PROJ IV in (2): references (357 b, c, d and 358).
- to no 4: Reaction of CS_2 with cyanides and dicyanogen, begun in 1938 (8).

Plate 3: Projects in future

Nr	Project	ref
1	N-rich high energy compounds according to <i>Formula Summary A</i>	(1, 2)
2	Higher silanes: Si >6 as rocket fuels	(9a,b)
3	protection against neurotoxines	(10)
4	2,4,6-trinitro-anisol chemistry	(11)
5	Ammoniumnitrate in plants like mosses	(12a)

commentary to Plate 3: (added later)

- to no 1: *Formula Summary A* in *Plate 1b*
- to no 2: Summary about the experiments to prepare higher silanes published in the internet, 2007 (9a)
Polysilanes are suitable as H_2 -reservoir and H_2 -carrier (9b)
- to no 3: Use of enzymes against warfare agent like fluorodiisopropylphosphate et al. : PROJ XVIII in (2)
- to no 4: Nitration of anisol (11): study to find the best conditions to prepare 2,4,6-trinitro-anisol (according to the author's opinion more interesting trinitrobenzene)
- to no 5: Lab report Feb 1943 (12a)

In the interview the author pointed out that he intended to synthesize *later in any case* the compounds listed in *Plate 1a* and *Formula Summary A (Plate 1b)* starting from the old publications written from J.Thiele, R.Stolle and co-workers 1892-98 and 1933. It would be interesting to combine N-rich high energy compounds with the classic NO₂-representatives which are as follows:

Compound types such as TNT (trinitrotoluene), hexogen (trimethylene trinitramine), i.e. those containing fuel-C and one or more oxidant group(s) in the form of NO₂.

According to a statement of the author in 1942 one can speak of NO₂-groups *as* nitro (C-N bond), nitrate (C-O-N bond), nitrimino (C=N-N bond), nitramino (C-NH-N bond) [N always being NO₂]

So far about the presentation speech (interview).

The first opportunities were offered soon *after* the author left the Army Research Establishment, namely at RUHRÖL, especially after he had met the Swiss engineer O. Matter, an expert on explosives, in 1943; cooperation from 1947; cf. "4a), Matter" in (1).

Continuation of the subject in Section II, 2.

The interview and the lectures went off well, but the author was unable to report for duty at the Army Explosives and Warfare Agents Research Establishment in Prague immediately, as he had not only to be discharged from hospital, but also released by the reserve unit. So the start of work in Prague was delayed until the beginning of 1943.

II

in Prague, 1943

The only task set for the author was to study the nitration of *m*-dinitrobenzene (I) to 1,3,5-trinitro-benzene (II) [and analytical determination of I and II including by-products].

Every organic chemist would say this is an old hat. The two directors of the institute were physical chemists, i.e. they had no experience in organic chemistry.

From the first day at the Prague "Research Institute", it became clear to the author that there was little interest in genuine research. All that mattered to the people there was to get through the war in the best possible way. Therefore, the author knew he would find time to pursue *his own interests*, i.e. to conduct experiments *apart from his duties*.

II 1

Duties at the Army Research Establishment

a) Nitration of *m*-dinitrobenzene (12b-f)

When the author was posted to the (German) Army Research Establishment for Explosives and Warfare Agents in Prague at the beginning of 1943, he was “assigned” to Dipl Ing A Kühnl, who had begun systematic investigations into the nitration of *m*-dinitrobenzene.

The author saw as already mentioned his first task in developing a *method to analyze* 1,3,5-trinitro-benzene in addition to *m*-dinitrobenzene. This was soon achieved using the method of polarography [proposed by the author who had already experience with the HEYROVSKI method, studying the polarographic behaviour (reaction) of halogenated hydrocarbons (12g)].

It was then possible – together with A.Kühnl – to try, in a series of experiments varying the nitration conditions, to improve the yields of trinitrobenzene (12d-f). The author discovered the formation of tetranitromethane as by-product (12b): Under very strong nitration conditions as high concentrated HNO_3 in presence of fuming SO_3 -containing H_2SO_4 - the starting material was attacked resulting in tetranitromethane. So the analytic method had to be amplified into determination of three nitrocompounds if possible next to each other *or* tetranitromethan separately from the other ones.

All experiments were carried out behind protecting iron plates. Mostly by the author himself and *all alone* because Kühnl chickened out with the flimsy “excuse” of having wife and children; cf. (12d)

The analytical method mentioned above was completed and perfected for use; results see next page (12c-f).

Only with reservations (which, however, could not be justified truthfully but only flimsy explanations) had the author collaborated on this task as it was “much too late” as at the time the second world war could already be considered lost for Germany.

Luckily “fate” put an end to continuing such ‘pointless’ experiments to improve the preparation method of the old and well-known explosive compound *s*-trinitrobenzene when the author was released in the framework of Hitler’s reallocation decree of 1943 from Prague to Bottrop in Westphalia, into fuel chemistry: “*Gasoline and armor have priority over explosives.*”

b) Results of the development of the polarographic identification of m-dinitrobenzene (I), 1.3.5-trinitrobenzene (II), and tetranitromethane (III) [Experimental data taken from ref (12c).]

Even when we carried the first nitrations of m-dinitrobenzene under stringent conditions with high-concentration acids (plus SO_3), we noted considerable losses in substance which caused us to look for nitrated C_1 and C_2 fragments; for example, the author discovered the formation of considerable amounts of tetranitromethane early on which was included in the analytics.

In order to complete the polarographic identification of I, II, and III, polarograms were recorded at different *pH* values:

Diagram 1: pure solutions of I and II,

Diagram 2: mixtures of I and II,

Diagram 3: III on its own,

- using the HEYROVSKI polarograph developed just then (1939) [sensitivity: $4.2 \cdot 10^{-5}$ ampere, 2 volt accumulator]
- using the data of L. KOLTHOFF and J. LINGANE (Polarography, N.Y. 1941) and M. SHIKATA and H. HOZAKI [Mem. Coll. Agricult. Kyoto University, vol. 17 (1951)]

Because of superimposition at step minus 405 - 415, it was not possible to identify III in a mixture with I and II at a *pH* value of 12, but only after it had been separated.

The reduction potentials of I, II, and III identified from the polarograms are summarised in Table 1.

In order to determine the reduction potentials, the potential of the *resting* Hg electrode was measured against a calomel electrode and the potential of the *drop* electrode calculated on this basis of this value. The drop time of the Hg electrode was always 1.5 to 2 seconds. In each case, polarography was carried out under nitrogen in a 5.0 ml solution. The solution with a *pH* of 12 had the following composition: 50.0 ml of 2n NH_4Cl , 2.0 ml of gelatine solution (5 %), 10.0 ml of 1n NaOH , 8.0 ml of H_2O . [Gelatine solution was added (adjusted to a *pH* of 12) to suppress maxima which would have occurred otherwise. Double gelatine content in case of III]. The basic solution invariably had a volume of 90 ml. For identification, 10.0 ml of the solution to be analysed were added.

The optimum *pH* value for the identification of I, II, and III was 12.

Diagram 1:

Polarogram of *m*-dinitrobenzene (I) and of *s*-trinitrobenzene (II) in the concentration 10^{-4} mol/L at different *pH*

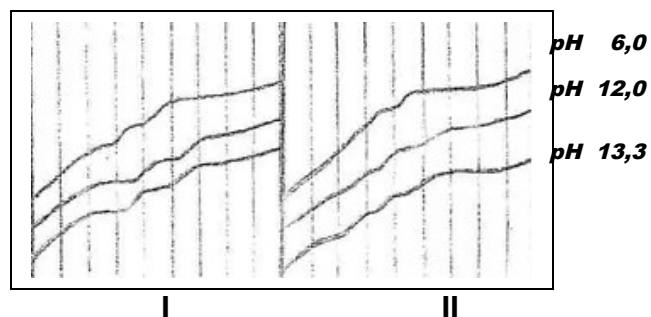
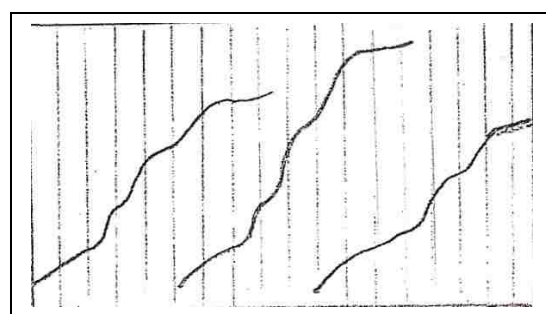


Diagram 2:

Polarogram of *m*-dinitrobenzene (I) + *s*-trinitrobenzene (II) at *pH* 12,0:



1 2 3
 curve 1: 0,5 10^{-4} mol/L I + 2,0 10^{-4} mol/L II
 curve 2: 2,0 10^{-4} mol/L I + 2,0 10^{-4} mol/L II
 curve 3: 2,0 10^{-4} mol/L I + 0,5 10^{-4} mol/L II

Diagramm3:

Polarogram of tetranitromethane at different *pH* in the concentration 10^{-4} mol/L

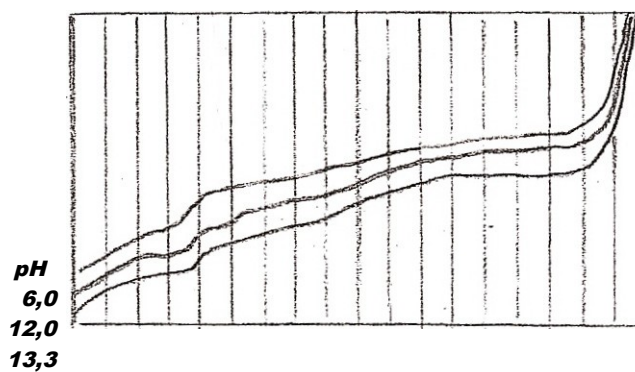


Tabelle 1:

Reduktionspotentiale (in Millivolt gegen 1 n-Kalomelektrode) von m-dinitrobenzene (I) s-trinitrobenzene (II) and tetranitromethane (III) - Konzentrationen 10^{-4} Mol/L

	<i>pH</i> 6,0	<i>pH</i> 12,0	<i>pH</i> 13,3
I step 1	-320	-440	-410
step 2	-470	-610	-580
II step 1	-260	-310	-310
step 2	-360	-440	-410
step 3	-470	-610	-580
III step 1	-220	-405	-425

When the *pH* value is constant at 12, the level of all reduction step varies in strict proportion to the concentration of I and II, respectively. In case of mixtures, we determined the content of II from the level of the first reaction step and the total of the content of I and II from the level of the other reduction steps: diagram 2.

III could be identified with the aid of diagram 3 after it had been separated from the nitration mixture (extraction and vacuum distillation at 60°C).

For further details regarding the application of these methods of analysis to the nitrations of I to II (and III) and the preparation of the solutions for analysis please refer to (12f).

Later on, the author had a method of analysis devised at UFSM in Brazil for studying the nitration of p-nitroanisol (IV) to obtain 2,4,6-trinitro-anisol (V): polarographic identification of IV and V; cf. (12k).

c) C_2Cl_2 and C_5Cl_6

On 8 Feb 43 the author had given a lecture, entitled "Comparison of "explosive" properties of C_2Cl_2 and C_5Cl_6 ". Results: C_5Cl_6 did not come to the expectations of the direction board of the institute: C_5Cl_6 was - contrary to C_2Cl_2 - n o t qualified as explosive; cf. also later lectures given there on 18 Feb and on 15 Mar 1943 to confirm the earlier results and to convince the disbelieving direction board (5b).

d) Nitration of anisol and *p*-nitroanisol

Seeing that it was impossible to increase the yield of 1,3,5-trinitro-benzene because of decomposition into tetranitromethane of the starting material we started anisol and *p*-nitroanisol nitration experiments - against the command of the chiefs - but these trials did not come to an end (11) because of the mentioned Hitler's reallocation decree of 1943. Experiments continued in Brazil from 1975 on (12k); cf also Plate 3, n° 4.

II 2

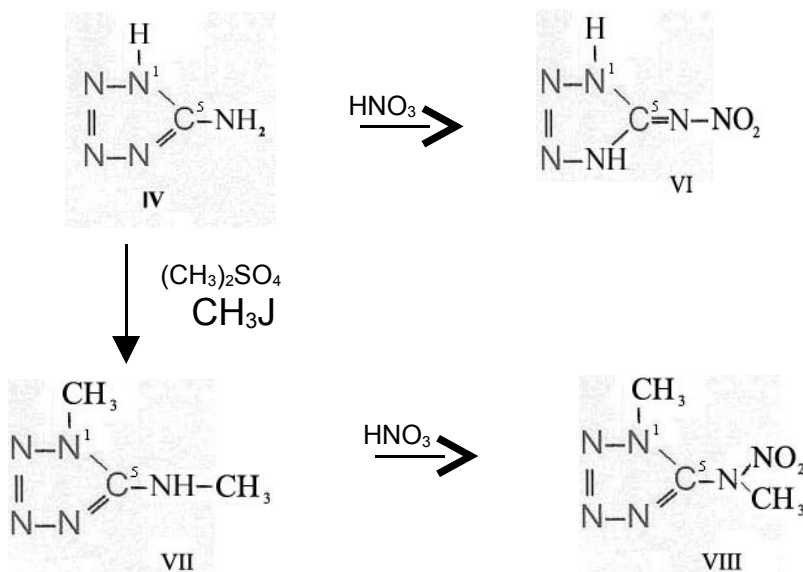
Own activities apart from the author's duties at the Army Research Establishment (spring '43) and experiments carried out between 1947 and 1956 – in co-operation with Dipl.Ing.O.Matter

a) still at the Army Establishment:

- continuing study the DIEN-synthesis of C_5Cl_6 ; cf. also PROJ XI (2,5b)
- starting the experiments regarding the nitration of 5-amino-tetrazol (IV) to VI and of 1,5-dimethyl-tetrazol (VII) to VIII (*Formula Summary B*) next page
- starting experiments to prepare 1,5-diamino-tetrazol (V) from thiosemicarbazid (*Formula Summary C: next page*)
- starting the preparation of higher silanes starting from chlorinated Si-compounds or from lower silanes (first pyrolytic experiments)
The author gave a report about "Synthesis of Silanes" in a colloquium at the Army Research Establishment [ref in (9a)]
- synthesis of 1,2,3-benzotriazole: Plate 2; cf. (12i,j)

Plate 4: Formula Summary B

**Nitration of 5-amino-tetrazol (IV) and IV-derivates i. e. VII to VIII
(experiments carried out in Prag 1943)**



IV synthesized according to J. Thiele

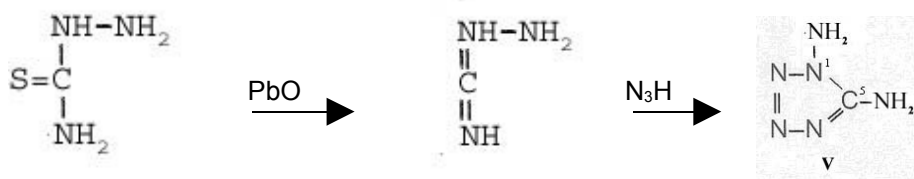
b) 1,5-Diamino-tetrazole

Research regarding 1,5-diamino-tetrazole (V) was started in 1943 in Prague, continued and finished 1953 in Switzerland together with Ing.O.Matter: *Formula Summary C*.

A new V-synthesis was found in 1972 in Brazil.

Plate 5: Formula Summary C

1,5-Diamino-tetrazol (V) starting from Thiosemicarbazid



Thiosemicarbazide was converted into 1,5-diamino-tetrazole (V) with PbO and NaN_3 in a CO_2 atmosphere via an intermediate with HN_3 . The Pb azide resulting as a side product causes problems and is therefore unsuitable for industrial use. Another method of production for V was desirable. V forms salts with perchloric acid and hydrogen azide.

III

In Berlin, Switzerland, and Brazil

An improved V-synthesis was successfully carried out in Brazil in 1972 in cooperation with the colleagues from CONSULTING DEVELOPMENT ENGINEERING and BRASTONE in S. Paulo, SP, and in Curitiba, PR, Brazil, listed below.

New synthesis of V:

Diazo treatment of diaminoguanodinium-halogenids in a narrow pH range 7,6-8,2 at room temperture (30-35° C).

Reaction dangereous: azid formation if pH not taken into consideration. To find out the best pH range we carried out 14 series experiments behind a protecting iron plate because of the expected azid formation.

The author owes thank to drs M M Faria, S.Paulo, SP, and F R Pessler, Curitiba, PR, for co-operation and their courage - 8 explosions!

Experimental Part

to 1,5-diamino-tetrazol (V) experiments

R.Riemschneider,1943 and R.Riemschneider,O.Matter, 1953

1,5-Diamino-tetrazol (V) and V-nitrat, V-perchlorat, V-azid

Patentapplication O.Matter, inventor: Riemschneider und Matter.

V was prepared in accordance with R. Stolle et al., J. Prakt. Chem. 1933, 138, 1. Because of the risk of explosion, very small batches were used to obtain sufficient V.

Preparation of 1,5-diamino tetrazole (V):

55 ml of an aqueous solution containing 4.5 g of diamino guadininium chloride and 1.5 ml of concentrated HCl are prepared under an exhaust hood behind an iron plate. Diazotisation with sodium nitrite is carried out under an N₂ flow at 2 to 4°C: 20 ml of nitrite solution containing 2.5 g of NaNO₃ are added dropwise with strict observation of the required temperature. After 45 minutes, the pH value of the reaction mixture is adjusted to 8.0 to 8.2 with Na₂CO₃ and stirred slowly at 45°C for 25 minutes, still under nitrogen. After that, the N₂ flow is concentrated *in vacuo* until dry (keep a safe distance!). After cooling, repeated extraction with a little ethyl alcohol at 60°C and recrystallisation from water as before is carried out. V mp 185°C (low yield).

A total of 19 serial experiments were required to determine the optimal conditions for preparing V. In the present case, we benefited from the experience with V gained as early as 1943 and in the 1950s. After a heavy explosion occurred during the second serial experiment, we worked with grip arms wherever possible, just as in our experiments with dichloroacetylene and monochloroacetylene [R. Riemschneider, A. Brendel, Liebigs Ann. Chem. 640, 1 - 15 (1961)] und in the nitration of meta-dinitrobenzene to form trinitrobenzene (12d); cf. Section II 1a).

V-nitrate

The formula to prepare is the same as indicated in the patent application of 1953. Observing the precautions specified above:

4 g of fresh prepared V are added to 3,0 ml of 66% HNO₃ at 20° C in N₂-stream and very slowly heated, then under cooling given to the clear solution ethylether in amount of 25-35 ml. The precipitated crystals are filtered off and washed with ether, dried over P₂O₅ after crystallisation from ethanol: 2,5g V-nitrate, mp 135-138°C.

V-perchlorate:

Observing the above precautions and working with grip arms, 2 g of V are dissolved in 25 ml of high-purity methyl alcohol. 1.5 g of concentrated perchloric acid are added gradually with slow stirring, still under nitrogen. After reacting at 20°C for 1.5 hours, the mixture is extracted with ethyl ether mp 97-98°C.

V-azide: high explosive, difficult to handle

V-preparation	CH₄N₆	100,07	calc.	C 12,0%, H 4,0%, N 84,0%
			found	C 12,2% H 4,0% N 83,8%
V-nitrate	CH₅N₇O₃	163,1	calc.	C 7,4% H 3,1% N 60,1%
			found	C 7,3% H 3,0% N 60,0%
V-perchlorate	CH₅N₆ClO₄	200,5	Calc.	C 5,9% H 2,5% N 41,9%
			found	C 5,8% H 2,9% N 41,6%

The explosive characteristics of these compounds prepared in Vitznau and Berlin in 1951 and 1952, V, V-nitrate and V-chlorate, were expertly tested by engineer O. Matter at the end of 1952 at his testing site for explosives on Vierwaldstättersee (near the Rütli field) and compared with TNT and the pentaerythrite nitric acid esters¹ we developed later. Data regarding the heat of explosion and detonation (P,D), stability (impact, heat, friction, electrostatics) were collected.

Result: V-nitrate and V-perchlorate are comparable with TNT.

Detailed experimental data are set forth in specification of the Swiss Patent applied for by O. Matter, inventors: R. Riemschneider and O. Matter. The letter from Mr. Matter to the author in December 1952 shown below expresses delight that both V-salts have explosive characteristics comparable with TNT.

Schlußbemerkung zu V und V-Salzen:

In der umfangreichen Publikation von Galvez-Ruiz et.al, Inorganic Chem.44,4237 (2005) sehen wir unsere hinsichtlich V und V-Salzen vor mehr als 50 Jahren erzielten Ergebnisse bestätigt.

¹ German Patent Application: File No. R 21634 IV b/12 o

Copy of the Matter letter dated December 2, 1954

**O. Matter, Certified Engineer
Vitznau, Switzerland**

**Dr. R. Riemschneider, University Lecturer
Berlin, Bolivarallee 8**

Dear Dr. Riemschneider,

**This is just a quick note to tell you that the test of the
diaminotetrazole salts for explosive characteristics produced a very
satisfactory result. They are comparable with TNT!**

**As discussed, we can now apply for a patent both for the method of
preparation and the explosive character. Applicant: O. Matter,
inventors: R. Riemschneider and O. Matter. My Swedish partners will
be delighted.**

I look forward to seeing you in Vitznau soon.

Vitznau, December 2, 1954, signed Matter.

Dipl.Ing.O.Matter
Vitznau, Schweiz

Herrn Dozent Dr.R.Riemschneider
Berlin, Bolivarallee 8

Lieber Herr Dr.Riemschneider,
rasch nur kurz die Mitteilung, dass die Prüfung der hergestellten
Diaminotetrazolsalze auf Sprengwirkung positiv verlaufen ist: Vergleichbar mit TNT!
Jetzt können wir Herstellung und Sprengstoffcharakter anmelden, wie
besprochen! Anmelder: O.Matter, Erfinder: R.Riemschneider und O.Matter. Meine
schwedischen Partner werden sich freuen.
Ich erwarte Sie bald in Vitznau.
Vitznau, 2.12.1954 gez.Matter

**As mentioned in earlier publications all the *necessary
precautionary measures* were taken for all experiments with high
energy compounds and also later for working with lost, saran
ecc.**

**We experimented with explosive compounds behind iron plates
constructing special protective devices like safety masks and
working with gripping tongs – similar to in the case of working
with chloroacetylenes, but in this case with long gripping tongs
ecc, all described in PROJ XII (2) and in SPECIAL PART E.**

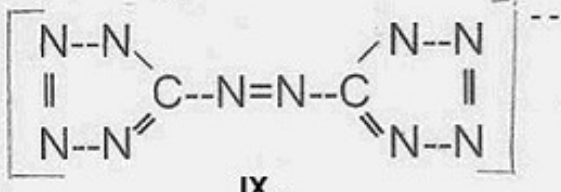
c) Azotetrazolate salts: Vitznau (1954) and Curitiba, S.Paulo (1980)

Azotetrazolat salts (IX) are formed according to J.Thiele [Liebigs Ann.Chem.270, 54 (1892);303,57(1898)] by alkaline permanganate oxidation of 5-amino-tetrazole (IV), precipitated as Ba-salts (IXa) which delivered with MgSO_4 and K_2SO_4 the corresponding IX-salts: *Formula Summary D*.

To increase the N-content we prepared IX ammonium- and hydrazinium salts like tetramethylammonium-IX (IXb from IXa), trimethylhydrazinium-IX (IXd) from IX-Ag (IXc) and iodide). The sensitivity of all prepared IX-salts to friction and shock depends on their rest water content. Data of explosive properties are secreted.

Plate 6: Formula Summary D

Azotetrazolate salts (IX salts)

 <p style="text-align: center;">IX</p>	IXa IXb IXc IXd	Kation Ba ⁺⁺ 2[(CH ₃) ₄ N] ⁺ 2Ag ⁺ 2[(CH ₃)N-N(CH ₃) ₂] ⁺
---	--------------------------	--

d) Dinitrobiuret (X)

In one of his lectures given in the seventies at the UFSM in Brazil, the author had discussed compounds rich in N as energy suppliers, including the dinitrobiuret (X) described by J. Thiele 1898 in Liebig's Ann. Chem. 303, 93 (1989); also see *formula scheme I* shown in this volume under IV, "Bonded to People", section K) (1).

Systematic investigations carried out by the author in 1957 and after 1970 included the starting substances cited in *Formula Summary E* and a few nitration products.

Plate 7: Formula Summmary E

Nitration products of urea (i.g. guanidin) and of related compounds like biuret and triuret: Dinitrobiuret (X), dinitrotriuret (XI) and dinitroguanidin (XII)

$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH}_2 \end{array}$	$\begin{array}{c} \text{NH-NO}_2 \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH-NO}_2 \end{array}$	$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{HN}=\text{C} \\ \diagdown \\ \text{NH}_2 \end{array}$	$\begin{array}{c} \text{NH-NO}_2 \\ \diagup \\ \text{HN}=\text{C} \\ \diagdown \\ \text{NH-NO}_2 \end{array}$
$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH} \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH}_2 \end{array}$	$\begin{array}{c} \text{NH-NO}_2 \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH} \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH-NO}_2 \end{array}$	$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{HN}=\text{C} \\ \diagdown \\ \text{NH} \\ \diagup \\ \text{HN}=\text{C} \\ \diagdown \\ \text{NH}_2 \end{array}$	$\begin{array}{c} \text{NH-NO}_2 \\ \diagup \\ \text{HN}=\text{C} \\ \diagdown \\ \text{NH} \\ \diagup \\ \text{HN}=\text{C} \\ \diagdown \\ \text{NH-NO}_2 \end{array}$
$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH} \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH} \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH}_2 \end{array}$	$\begin{array}{c} \text{NH-NO}_2 \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH} \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH} \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{NH-NO}_2 \end{array}$		

Decomposition temperature

dinitrobiuret,	$\text{C}_2\text{H}_3\text{N}_5\text{O}_6$	90-130°C (depending on increase of heat)
trinitrobiuret,	$\text{C}_3\text{H}_4\text{N}_6\text{O}_7$	(not determined)
dinitroguanidine,	$\text{C}_2\text{H}_5\text{N}_7\text{O}_4$	(not determined)

e) 1,1-diamino-2,2-dinitro-ethylene (XI) - ref. (12h):

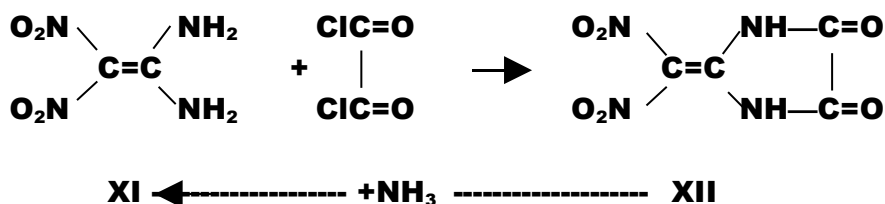
As repeatedly mentioned above, the author cooperated with the engineer O. Matter from Vitznau, Switzerland, in several fields. In 1947, Matter approached the author with the request to jointly investigate the reactivity of the above-mentioned compound XI, especially with the objective of finding an effective XI synthesis. A Swedish company in the background was interested in explosives and was willing to provide 25 g of XI.

The author included XI in his current acylation experiments of PROJ I; i.e. acylations of XI with alkylhalogenides, oxalyl chloride, malonic acid dichlorid etc. We expected in the case of the use of oxalyl chloride the formation of the *imidazole* derivative: 2-dinitromethylene-*imidazolidine*-4,5-dione (XII). The Swedish Company had prepared XI by nitration of 2-methyl-*imidazole*.

As shown in *Formula Summary F* the acylation of XI with oxalyl chloride resulted in fact in XII. Treatment of XII with NH_3 led back to XI in high yield - a very interesting reaction keeping a new XI-synthesis in mind: A suitable way of another XII-synthesis was demanded and had to be found *via* an imidazol derivative.

Solution shown in *Formula Summary G*: Reaction of acetamidine chloride with oxalic acid dimethylester led to XIII and whose nitration with $\text{HNO}_3/\text{H}_2\text{SO}_4$ to XII and with NH_3 furtheron to XI (12h).

Plate 8: Formula Summary F



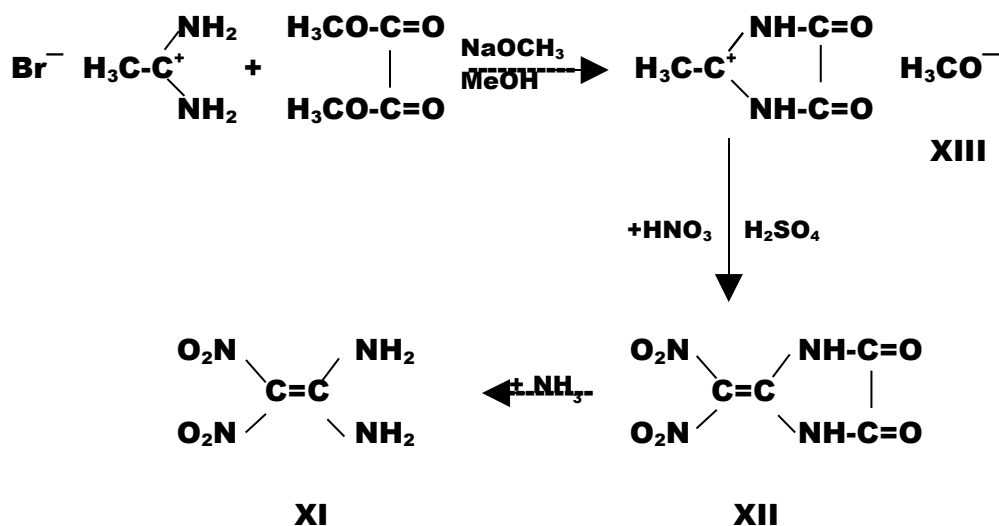
XI delivered and XI prepared from XII are identical: yellow colour, recrystallized from dimethylsulfoxide (Swedish proposal), decomposition temperature: circa from 200°C on until 230°C.

The reactions of XI with acyl bromides and -chlorides resulted only in monoacyl-derivatives: acetyl-XI, propionyl-XI (12h).

All XI-acylation experiments are conducted between 1947 and 54 in Berlin, partly in co-operation with Ing. C.Brandmayer.

Plate 9: Formula Summary G

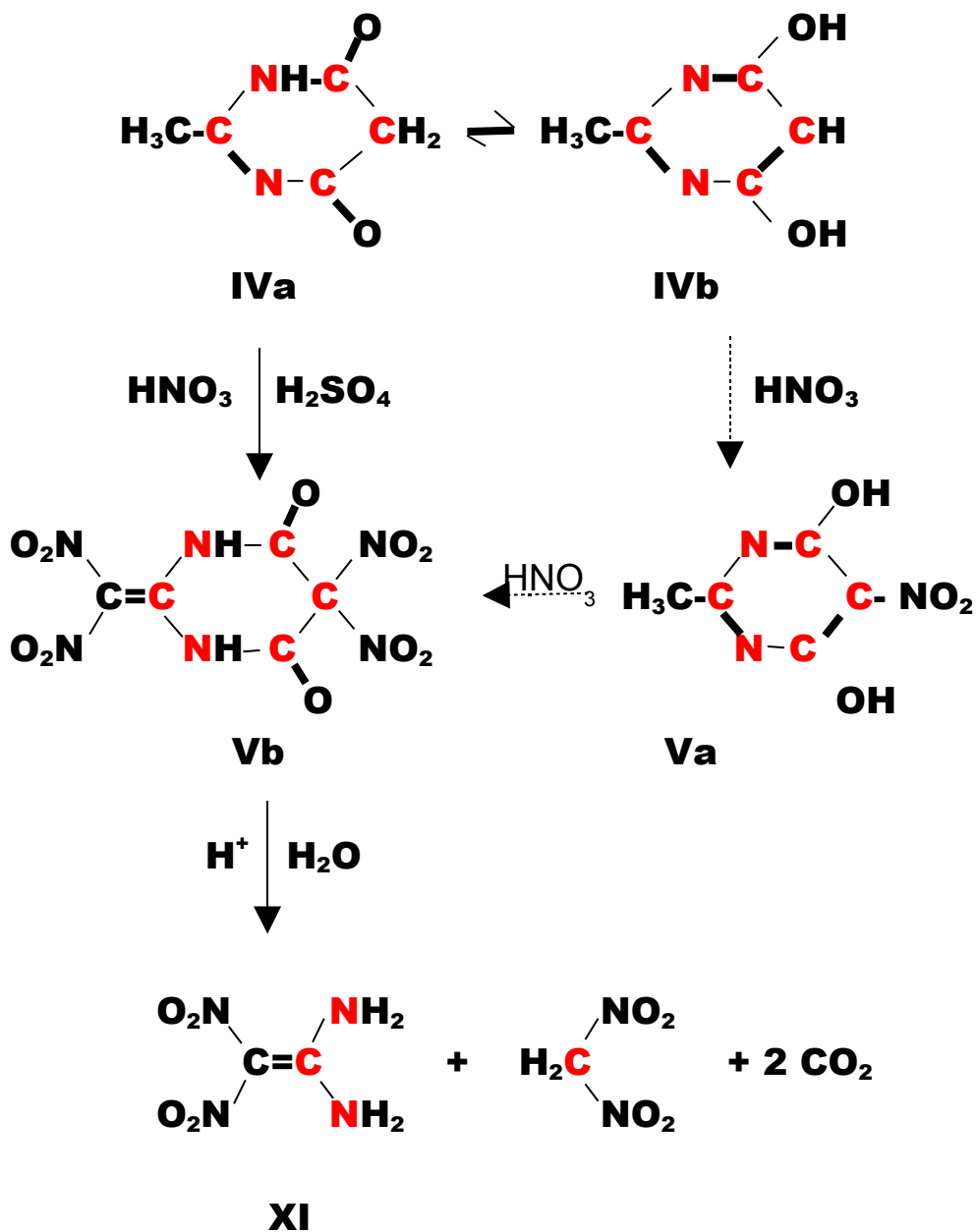
Second synthesis of 1,1-Diamino-2,2-dinitro-ethylene (XI)



Synthesis developed 1956 by R.Riemschneider, O.Matter, C.Brandmayer in co-operation with a Swedish company specialized in explosives.

At the time, we had considered another possibility of an XI synthesis which is shown in *Formula summary H*. The 5-ring compound XIII set forth in *Formula summary B* has been replaced by a suitable six-ring compound in H, namely a pyrimidine component.

Plate 10: Formula summary H



IV (in trade) is nitrated to “Vb” and “Vb” hydrolized to XI + CO₂ + dinitromethane (unfortunately formed in big quantities). The formulated nitro-compounds “Va” and “Vb” are not isolated.

We started orientation experiments to this *Formula Summary* in 1956, but only in the 70ies we succeeded to prepare XI from IV.

We also tried from 1956 on (until 1995) to synthesize the in *Formula Summary J* formulated *cis*- and *trans*-XI-isomers – unfortunately without success.

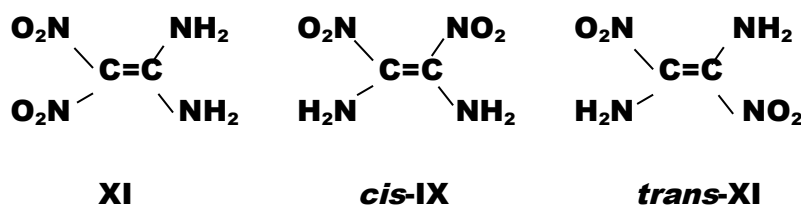
To pursue this research for the two geometric isomers the author had several reasons:

- 1) It would have been interesting to find out if they were more or less energetic and if they were more stable than XI.
- 2) The isomers would have been useful in the frame of the project *cis-trans*-asymmetrie, especially because we found that only one amino group of XI is normally reacting in acylation experiments (12h); see PROJECT I 2,1 point 12 and

<http://www.bwvsociety.org/journal/html/stereochem.htm> 2006

Plate 11: Formula Summary J

Isomers of 1,1-diamino-2,2-dinitro-ethylene (XI): *cis*-1,2-diamino-1,2-dinitro-ethylene (*cis*-XI) and *trans*-1,2-diamino-1,2-dinitro-ethylene (*trans*-XI):



SPECIAL PART A

„Weg“ bzw „Umwege“ :

getting away from the front and working as a chemist

At this point it should be explained how and why the author ended up at the (German) Army Explosives and Warfare Agents Research Establishment in Prague or - more accurately Below, the author explains

- **how he ended up in explosives research in view and despite of his negative attitude towards the NS system**
- **how he set about getting away from the front and working as a chemist. Brief details of the roundabout route follow [*"Route" and "Detours" are briefly outlined*]**

The author had studied chemistry, completely in four trimesters and one semester, from 1939 to 01 Oct 1941 in Göttingen, Hamburg, and Leipzig including Diplomarbeit and Diplom-chemiker-Hauptexamen.

So as not to waste all that much time with the active military service¹ forced on the author from 03 Oct 1941, ie in order to be able to work in his vocation and gain professional experience, his father² had submitted an application to the (German) Army High Command (OKH stands for Oberkommando des Heeres) to employ his son as an army chemist. The information the Army High Command received from the referees given in the application (Prof C Weygand of Leipzig and Prof H H Schlubach of Hamburg, who both knew the author well since 1937 and had kept an eye on him) contributed - as the author later learned - to the positive decision. The order to report to Army High Command in Berlin [by-passing the reserve unit in Besançon / France he would normally have been posted to on discharge from hospital] for an interview, including giving lectures, immediately after convalescence reached the author 1942 while he was in the military hospital in Furth im Wald.

¹ Even at the time, the author considered the war lost, even more so after America entered the war in Dec 41 (Germany was already at war with the USSR from 22 June 41). Napoleon's failure at the beginning of the 19th century had clearly been completely forgotten.

² For obvious reasons, the author was well-advised not to submit the application himself. During the year, the Army High Command had tried to contact the author several times via company HQ, but Captain Schauerhammer and the company sergeant-major Schwartz had swept it under the carpet every time. Contact was only established via a doctor at the military hospital.

SPECIAL PART B

"The chemical warfare agents": Table 2'

The subject of the lecture I "The chemical warfare agents" (3) given by the author in Berlin on 21 Dec 42 was set by the Army High Command when in November he was ordered to report for possible indentation as an army chemist. It now paid off that the author had attended a compulsory lecture on warfare agents given by Prof Dr J Goubeau in Göttingen in the winter trimester of 1939 which dealt with about half the compounds dealt with in the author's own lecture: Tab 2.

From the lecture itself:

"The year of birth of the gas weapon is 1912 [not 1914 in Ypres, as people like to state], its 'place of birth' Paris, to be more precise bromoacetic ester was tested in the Paris municipal laboratory and introduced as a warfare agent. It was then first used in 1914 in rifle grenades in the Battle of the Argonne Forest. The compounds proposed, tested and deemed suitable in the years 1912 to 1920 are collated in Table 2, previously mentioned - giving physical and physiological indices. All of the compounds declared here as warfare agents were known in the literature and not discovered for the purposes of gas warfare" [unlike the nerve gases based on phosphoric acid esters developed in Elberfeld in the 40s].

Some of the coefficients used in the head of Table 2: "The principal warfare agents (1912 - 20)" require explanation. The author uses the definitions given by Prof Goubeau.

col 7: *Harassment level* [untere Reizgrenze] **Tab 2**
reached if a state of irritation, that can consist of sore eyes, itching or burning in the nose, or a sore throat is perceptible after one exposure.

col 8: *Intolerance level* [Unerträglichkeitsgrenze] **Tab 2**
also expressed in mg warfare agent per m³: the limit is reached if the level of harassment forces flight within one minute (if free to do so).

¹

Key to Tab 2 supplemented in Nov 49. Lecture later given several times while teaching at UFSM (1972 - 80)

col 9: *Toxification index* [Tötlichkeitsprodukt, Vergiftungszahl ct Produkt]
Tab 2

„concentration“ x „survival time“ = toxification index

HABER and FLURY's ct product, the product of concentration and time: $c \times t$ (c in mg / m^3 , t in min), deduced from experiments with animals (dogs, monkeys). This is not a scientifically exact index but a relative value for the purposes of comparison.

col 10: *The danger index, warning index* [Gefährlichkeitszahl, Warnzahl] **Tab 2**

is the quotient of the ct product and the intolerance level. The higher it is, the more the harassment exceeds the poisoning action [col 9 : col 8].

Two examples to illustrate irritant and toxicant:

Example 1: The typical irritant bromomethyl ethyl ketone (Tab 2, ser n° 10) has a lachrimatory effect at $1.6 \text{ mg}/\text{m}^3$, the incapacitation limit is $16 \text{ mg}/\text{m}^3$. The ct product is approx 6000: ie $6000 \text{ mg}/\text{m}^3$ inhaled for 1 min, or $600 \text{ mg}/\text{m}^3$ for 10 mins or $60 \text{ mg}/\text{m}^3$ for 100 mins all have the same lethal effect.

The danger index (quotient of ct product and intolerance limit) is thus $6000 : 16 = 375$. This means that a 400x concentration of the intolerable quantity is lethal in 1 min, or that the intolerable quantity must be inhaled for 400 mins to have a lethal effect.

Example 2: Perchloroformic acid ester, diphosgene (Tab 2, ser no 18) is a typical toxicant. Its harassment level is $5 \text{ mg}/\text{m}^3$, ie this concentration will cause sore eyes and throat, but is still tolerable. The intolerance limit is $40 \text{ mg}/\text{m}^3$, the ct product is 300. Inhaling $300 \text{ mg}/\text{m}^3$ for 1 min can have a lethal effect, ie the 8x quantity of the intolerable is lethal.

Some interesting facts about the 32 warfare agents listed are in the key to Tab 2.

There is a historiographic chart of when the individual warfare agents appeared, their use and duration of application in Table 3.

Table 2: The principal warfare agents (1912 - 20)^{a, b}

1 11	2	3 12	4	5	6	7	8	9	10	
Lfd. Nr.	Chemische Bezeichnung	Decknamen Trivialname	Sdp. °C	flüchtig bis 20°C	Spez. Gew.	untere Reizgrenze	uner- trägl.	Tödlich- keitsprod.	Gefährlich- keitszahl	Physiol. Angriffspunkt
			(mm)	Menge/m³		mg/m³	mg/m³	ca.	(Warnzahl)	
ca. mg										
1 ^c 30	Diphenyl- arsincyanid	Clark II Blaukreuz	360	0,1 mg		0,01	0,25	} 4 000	16 000	Schleimhaut der der tieferen Rachen, Luftröhre, und
2 ^d	Diphenyl- oberen sowie aminarsin- Luftwege (Nase, chlorid Bronchien	Adamsit ----	410	0,02 mg		0,01	0,4			
Lungenschleimhaut)										
3 ^c 30	Diphenyl- arsinchlorid	Clark I Blaukreuz	333	0,3 mg	1,4	0,01	1,0	4 000	4 000	
4 ^e	Chloraceto- Rachen, Lunge phenon	CN-Stoff 25	247	105 mg	1,3	0,3	4,0	4 000	1 000	
5 ^e	Bromaceto- Rachen, Lunge phenon	bis 30	254 Fp 50°	110 mg		0,3	6,0			Auge, Nase,
6 ^f	Ethyl-di- Luftwege chlorasin	Dick 24 Grünkreuz 3	156	22 g	1,68	0,1	10	3 000	300	obere u. tiefere
7 ^g	Bromaceton Atmungsorgane	B-Stoff 33	126	75 g	1,6	1,0	10	4 000	400	Auge, sodann
8 ^h	Jodessig- Atmungsorgane ester	Bretonite 12	180	3,1 g	1,8	1,4	15	1 500	100	Auge, sodann
9 ⁱ	Xylylbromid Atmungsorgane	T-Stoff 50	210-220	0,6 g	1,4	1,8	15	6 000	400	Auge, sodann
10 ^j	Brommethyl- Atmungsorgane ethylketon	Bn-Stoff Homomar- tonite	145	60 g	1,43	1,6	16	6 000	375	Auge, sodann
11 ^k	Phosgen bes. Lunge, Augenschleimhaut	Collongite 3 „Zusatz“	+ 8	Gas	1,4	5	20	450	22	tiefere Luftwege, daneben
12 ^l	Methyl-di- Luftwege chlorasin	Grünkreuz- 25 Kampfstoff	132	75 g		2	25	3 000	120	obere u. tiefere
13 ^m	Phenylcarbyl- Luftwege aminchlorid	„Weißkreuz- 25 Kampfstoff“	210	2,1 g	1,35	3	25	3 000	120	Auge sowie
14 ^h	Benzyljodid auch Luftwege	---- 25	226	1,2 g	1,54	2	30	3 000	100	Auge, daneben

15 ⁿ	Brombenzyl- auch Luftwege cyanid	„CA“ 60 Camite	225 (Z.)	0,7 g	1,54	0,3	30	7 500	250	Auge, daneben
16 ^o	Methyl- (schneidender Schmerz) schwefel- säurechlorid	Vaillan- tite	133 15	60 g		8	50	2 000	40	Auge daneben Luftwege
17 ^p	Bromessig- Luftwege ester ähnlich dem	---- 25 15	168	----	1,5	10	40	3 000	75	Auge, auch Auge sowie Lunge Phosgen
18 ^r	Perchlor- bes. Lunge, ameisen- säureester	Bisphosgen 4 oder Perstoff „Surpalite“ Grünkreuz	128	26 g	1,65	5	40	300	8	tiefere Luftwege, daneben Auge
19 ^s	Dichlordi- Nervensubstanz methylether (Gleichgewichtsstörung)	---- 4	105	180 g	1,37	14	40	500	12,5	Auge, Luftwege,
20 ^o	Ethyl- Luftwege schwefel- säurechlorid	Sulvinite 25	153	----		2	50	3 000	60	Auge u.
1	2	3	4	5	6	7	8	9	10	
11		12								
21 ^t	Chlorpikrin Lunge ähnlich	Klop, 2 -Aquinite, „NC-mixture“	113	180 g	1,69	2	50	2 000	40	Auge sowie dem Phosgen
22 ^u 15	Acrolein	Papite	52	----	0,80	7	50	2 000	40	Auge u. Lunge
23 ^v	Bromcyan Nervensubstanz	„Ce“ 25 Campiellit	61	200 g		5	60	2 000	33	Auge, Rachen,
24 ^u	Benzyl- Luftwege bromid	Cyklite 50	201	2,4 g	1,40	4	60	6 000	100	Auge, daneben
25 ^w	Perchlor- Luftwege methylmer- captan	„Clairsite“ 25	149	18 g	1,71	10	70	3 000	42	Auge u.
26 ^s	Dibromdi- Nervensubstanz methylether	---- 3	155	31 g		20	50	400	8	Auge, Lunge,
27 ^g	Chloraceton Luftwege	Tonite 25	119	120 g		18	100	3 000	30	Auge u.
28 ^x	Chlorvinyl. Zellgift dichlorarsin	LEWISIT 12 (Todestau)	190	0,4 g	1,26	ohne Warnreiz		1 500	1 : ∞	allgemeines
29 ^y	Dichlordi- Zellgift	LOST ^{y)} 12	216	0,6 g	1,26	ohne Warnreiz		1 500	1 : ∞	schwerstes allg.

•

^{y)} cf. also

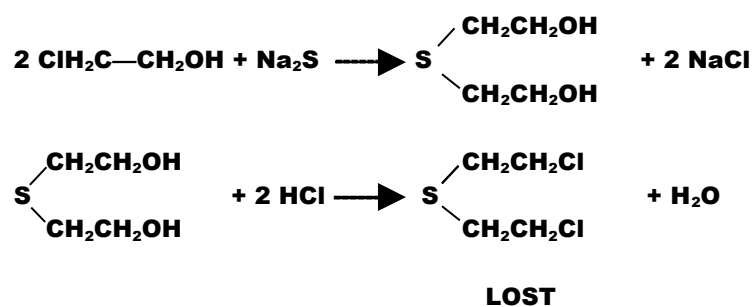
PROJ XVIII (2)

	ethylsulfid	Gelbkreuz- Mustard-Gas, Senfgas, Yperit							
30 ^z	Dimethyl- Schleimhäute, bes. sulfat	Rationit Lunge	188 12	3,3 g	1,32	ohne Warnreiz	1 500	1 : ∞	alle
31 ⁱⁱ	Chlor Luftwege, Auge	Berthollite 60	- 33,6	Gas		10 100	7 500	75	sämtl.
32 ⁱⁱⁱ	Blausäure Nervensubstanz		30	Gas		ohne Warnreiz	1 000 bis	1 : ∞	

Key to Table 2:

- a Continued in PROJ XVIII: tabun, sarin, soman etc
- b Definition of terms "harassment level" etc in col 7 - 10 (explanation in text)
- c Chlorarsinkampfstoffe (chloroarsine warfare agents) [Clark]: Clark I (C₆H₅)₂AsCl; Clark II (C₆H₅)₂AsCN, part of blue-cross group
- d Adamsit, named after the American chemist ADAMS although, according to German patent DRP 281049, this warfare agent was already synthesized in 1915 from AsCl₃ + diphenylamine [cleaving off 2 mol HCl]: mp 195°C. Part of blue-cross group.
- e C₆H₅COCH₂Cl, first produced by GRAEBE in 1869; typical irritant, rel low toxicity. Used by police as tear gas, by military as manoeuvre gas. Similar effect to bromoacetophenone.
- f C₂H₅AsCl₂ from ethylarsine oxide + HCl; former from diethyl sulphate + ethylarsinic Na and reduction with H₂SO₃ (American technique). Dick, part of green-cross-group
- g H₃CCOCH₂Br (French: blotite or martonite). Like Cl analogue: irritant, low toxicity.
- h H₅C₂OOCCH₂I, further iodine compounds: iodoacetone and benzyl iodide gained no great significance
- i I-Stoff, derived from Dr Tappen, not from tear gas. Strong irritant, smells of lilac (German: Flieger, hence "Fliegergas") when diluted. Mixture of isomers. Replaced by phenylcarbamoyl chloride [Phenylcarbamylchlorid].
- j H₅C₂COCH₂Br, introduced due to a lack of acetone.
- k COCl₂, known since 1811 (DAVY), from Cl₂ + CO in the presence of carbon (DAVY: in sunlight). Also obtainable from fuming H₂SO₄ and boiling CCl₄: CCl₄ + SO₃ → COCl₂ + SO₂Cl₂
More than 80% of all gas fatalities in WW I were victims of phosgene, the most perfidious and feared warfare agent of the time, acts as irritant and toxin, mainly the latter.
- l H₃CAsCl₂, aka methyl dick, cf f. Discovered by BAYER in 1850: irritant, very considerable combat strength, part of green-cross-group.
- m C₆H₅NCCL₂, obtained by chlorinating phenyl mustard (seed) oil, obtained from aniline and CS₂ at the time.
Also used to mask mustard gas.
White cross warfare agent, as shells marked with white cross to tell explosive and tracer munitions apart. [*Zur Unterscheidung von Brisanz und Buntkreuz-Munition*]
- n C₆H₅CHBrCN, by brominating benzyl cyanide in light, in pure state mp 29°C; distillation only possible in vacuum: 130°C (12 torr).
- o ClSO₂OCH₃ from SO₂Cl₂ + methanol. The ethyl analogue was introduced under the code name Sulvinite, obtainable from ethanol and chlorosulphuric acid - both used in mines.
- p Introduced at the suggestion of the Paris municipal laboratory in 1912.
Used to arrest the Bonnet Aachen gang near Choisy-le-Roy the same year (military helped).
Chloroacetone used from Nov 1914 due to lack of bromine, cf g.
- r ClCOOCCl₃, bisphosgene obtained starting from monochloroformic acid methyl ester (from COCl₂ + methanol) by chlorinating via the di- and trichloroformic acid methyl esters ClCOOCH₂Cl and ClCOOCHCl₂ through final chlorination in mercury light as a completely chlorinated compound particularly resistant to H₂O.
Perstoff has a propensity to split up into two phosgene molecules, aka diphosgene.

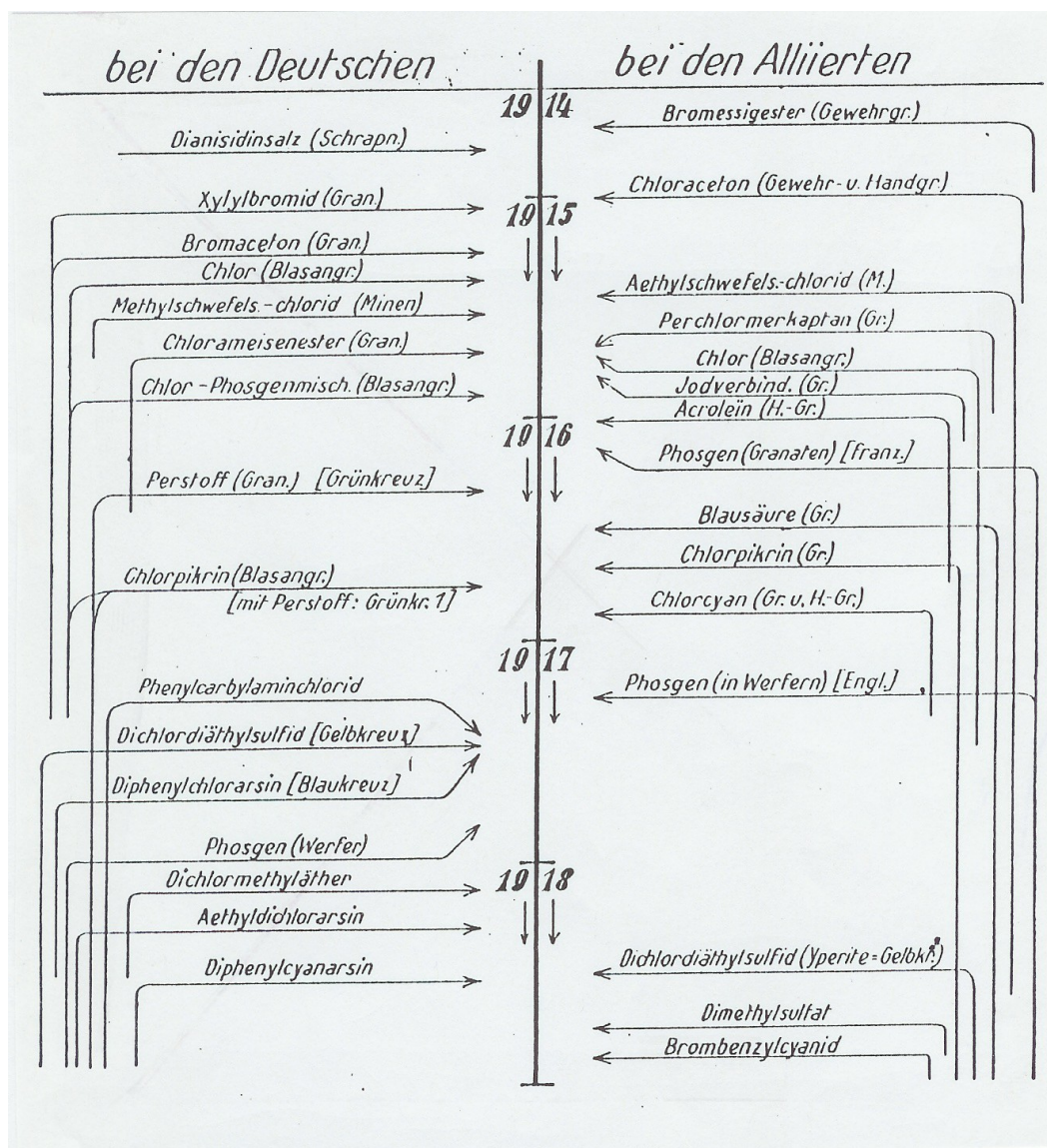
- s The harassment level of its bromine analogue, b p 155°C, is 20 mg/m³, 50 mg/m³ are intolerable, 400 mg/m³ are lethal.
Danger index: 8.
- t O₂NCCL₃, known since 1884, is obtained by the action of chlorinated lime on picric acid (equation); Klop can be steamed out of the mix of the two substances. Propensity to explode if heated suddenly. It was first used by the Russians in 50% solution with SO₂Cl₂ in shells in 1916. Almost as dangerous as phosgene.
Eq: C₆H₂(NO₂)₃OH + 11 Cl₂ + 5 H₂O → 3 O₂NCCL₃ + 13 HCl + 3 CO₂
Chlorination with eau de javel: aqueous KOCl solution with 80 - 145 g chlorine / litre.
- u insignificant.
- v BrCN, strongly irritant, similar to the French cyanogen chloride.
- w ClSCCl₃ from chlorine and CS₂ (iodine catalysis), insignificant.
- x CHCl=CHAsCl₂, Lewisit, from acetylene + AsCl₃ [in presence of AlCl₃], named after its discoverer LEWIS (USA), not used in WW I. Journ Chem Soc Apr 1921. By-products are: (CHCl=CH)₂ = AsCl and (CHCl=CH)₃As. It smells of geraniol, similar effect to LOST: destroys the skin.
- y LOST, named after LOMMEL and STEINKOPF, produced according to NIEMANN from ethylene and disulphur dichloride, smells of horseradish. V MEYER obtained the compound from HCl + thiodiglycol in 1886, these days as per equations:



Further details on LOST (mustard gas, yellow cross, yperite) in PROJ XVIII in (2).
Own experiments with LOST in PROJ XVIII (2); see (12L) and next page but one.

- z O₂S(OCH₃)₂ from methanol + chlorosulphuric acid, powerful toxic effect on all mucous linings, has caused many accidents in labs.
- ii classical warfare agent, discovered by SCHEELE in 1774, traded in steel cylinders.
Yellow liquid at 6 at: 1 l liquid chlorine, D 1.46, gives 643 l chlorine. Gas 2.5x heavier than air.
- iii considered one of the most terrible gases. Proposed by a Berlin pharmaceutical chemist as a "warfare agent" in 1813 when the French were threatening Berlin, although HCN is not suitable as a warfare agent in practice, as was later recognized.

Table 3: Chemical warfare agents (1914 - 18): chronology of first appearance, delivery system and period used



Germans: dianisidine salt (shrapnel) / xyllyl bromide (shells) / bromoacetone (shell) / chlorine (wind-borne) / methylthiochloride (mines) / chloroformic acid ester (shell) / chlorine – phosgene mix (wind-borne) / "surpalite" (shell) [Grünkreuz] / chloropicrin (wind-borne) [with "surpalite" = Grünkreuz 1] / phenylcarbylamine chloride / dichlorodiethyl sulphide [yellow cross] / diphenylchloroarsine [blue cross] / phosgene (mortar) / dichlorodimethyl ether / ethyldichloroarsine / diphenylcyanoarsine

Allies: bromoacetic ester (rifle grenade) / chloroacetone (rifle grenade, hand grenade) / chloroethyl sulphate (mine) / perchloromercaptane (shell) / chlorine (wind-borne) / iodine compounds (shell) / acrolein (hand granade) / phosgene (shell) [French] / Prussic [hydrocyanic] acid (shell) / chloropicrin (shell) / cyanogen chloride (shell and hand grenade) / phosgene (mortar) [England] / dichlorodiethyl sulphide (yperite = yellow cross) / dimethyl sulphate / bromobenzyl cyanide

Own experiments with warfare agents like LOST, TABUN ecc

Verfasser hat nach dem Kriege 12 Jahre in Berlin für das Verteidigungsministerium der BRD (Bonn) gearbeitet. Da auf Grund des Kontrollratsgesetzes (Viermächtestatus) in Berlin nicht direkt mit einem Ministerium der Bundesrepublik zusammengearbeitet werden durfte, waren einige Instanzen zwischengeschaltet: Für die gestellte Aufgabe brauchte es einen erfahrenen Chemiker.

Instanzenweg:

Das Verteidigungsministerium der BRD hatte eine Schutzkommission ins Leben gerufen, der der Pharmakologe Professor Dr Lendle, Göttingen, angehörte; dieser operierte mit dem erfahrenen Giftgas-Experten Dr.Schmidt, in Fachkreisen Onkel Otto genannt (wohhaft in der BRD und Berlin(WEST)), und dieser wandte sich auf Empfehlung der Firma AUER, Berlin, an Verfasser, um die von Verteidigungsministerium in Auftrag gegebenen Forschungen durchzuführen. Berichte des Verfassers dann über Onkel Otto, Lendle und Schutzkommission an das Ministerium.

Es handelte sich um das Auffinden und die Entwicklung von Materialien, die zur Anfertigung von Schutzanzügen und Gasplanen geeignet sind, d.h. undurchlässig speziell für Kampfgase wie Lost und die Nervengase Tabun, Sarin ecc.. Verfasser postulierte folgende Aufgaben:

- **Permeationsstudien an Hochpolymeren aller Art,**
- **Beschaffung bzw.Herstellung von Hochpolymer-Folien,**
- **Entwicklung von Messmethoden zum Studium der Durchlässigkeit von Lost und Nervengasen durch Hochpolymere: chemische, dielektrische, gaschromatographische Methoden**
- **Installation von geeigneten Laborräumen, z.B. auf dem Berliner Sprengplatz im Grunewald**
- **Beschaffung von LOST und Nervengasen durch „Onkel Otto“**

Allgemeine Formulierung des Themas: *Systematische Studien der Permeation kleiner Moleküle durch Polymere*, ein Thema, das Verfasser noch viele Jahre, vor allem in Brasilien an der UFSM, weiterverfolgt hat, nachdem das Verteidigungsministerium die Finanzierung eingestellt hatte und nachdem das Sprengplatzlabor in Berlin „aufgegeben“ werden musste:

Die genannten Forschungen wurden eingestellt, nachdem in der BRD Ende der 60er Jahre die „supersozialistische Ära Brandt“ begonnen hatte – eine Regierung, die in den 70er Jahren mit der diplomatischen Anerkennung der sog. DDR den 1848 geprägten „Deutschland-Begriff“ aufgegeben hatte, getreu dem damaligen Wahl-Slogan: „Wählt Brandt und Wehner und Deutschland wird kleiner“. Glücklicherweise wurde dann, 1989 durch die Bemühungen der Präsidenten Reagen und Gorbatschow die fast zementierte Teilung Deutschlands wieder rückgängig gemacht.

In PROJ XVIII „Permeations-Studien“ hat Verfasser über die entwickelten Permeationsmethoden und die Messergebnisse berichtet. Von allen getesteten Polymeren hatte sich *Teflon* als am widerstandsfähigsten gegenüber den Nervengasen und LOST erwiesen (12L). Inzwischen selbstverständlich, vor 50 Jahren aber neu. Heute ist das Tetrafluorethylen allgemein als widerstandsfähiges Material bekannt.

SPECIAL PART C

Lecture "*Chemical propellants for rockets*" (4)

given to staff officers in lecture hall of (German) Army High Command (*OKH*) in Jebenstraße, Berlin on 20 Dec 42, chair: Major Kassuba.

Ms 14 p + 12 slides, later completed into lecture in Vitznau in Switzerland, Dec 56

R Riemschneider (lecturer), O Matter

Completed lecture: "*Rocket propellants: (Raketentreibmittel)*

a) chemical propellants b) nuclear propulsion (atomic energy) c) other types of propulsion: ions, free radicals, photons, solar energy" given to a group of experts (primarily from Sweden) in Vitznau, Switzerland in Dec 56. Organized by Dipl Ing O Matter, explosives expert.

From the ms of Dec 56 lecture, 24 p: [The remarks made in the presentation to the (German) Army High Command in Dec 42 and the results from [(840) in (2)] were included in the lecture]

Here are a few main points from the content of the lecture:

The chemical reaction between molecules is at present (1956) the only type of rocket propulsion that works in practice.

We discussed known and new rocket propellants as well as the particular problems of *rocket control systems* in detail.

Further topics:

Developing faster means of transport. Research into possible new propellants should not initially take questions of cost into account. Results from intensive research work worldwide were pointed out, as well the limits. Intercontinental missiles will need to be fitted with multistage rockets. The limits of chemical propellants can be calculated. Exploration of interplanetary space will not be possible without other sources of energy.

The particular results obtained with dichloroacetylene as a jet engine fuel additive (840) were presented in the last part of the lecture. Regarding the continuing research about silicon hydrides as rocket propellants cf. recent publication in internet at <http://www.bwwsociety.org/journal/html/silanes.htm> 2007

SPECIAL PART D

Documents for OKH

In Dec 1942, after the interview in Berlin, the author handed over to Major Kassuba the following documents (b-d with permission of Profs Dr. C. Weygand and Dr. H. Kautsky):

- a) Ms of 20 and 21 Dec 42 lectures **SPECIAL PART B and C** including *Formula Summary A* plus slides.
- b) Lab reports taken from final year's work in chemistry at Matthias Claudius College in Hamburg-Wandsbek, submitted in Jan 39, on "Conversion of carbon disulphide with alkali cyanides to $C_4N_2S_2Na_2$ " and consecutive reactions (8).
- c) Lab report on "Preparing chlorothiopentafluoroethylene" (6) cf. also **PROJECT XII 4.2** in (2)
- d) Ms of work in field of "chloromethylthiochloride chemistry" (7) and also **PROJECT XII 4.1** in (2)
- e) plans for own experiments, incl. silicon hydrides and $HSiCl_3$; cf. (9a)
- f) report on 1,2,3-benzotriazol as the author's first example for N-rich high energy compounds (12i) – **PROJ. IV**

SPECIAL PART E

Precaution measures

We experimented with explosive compounds behind iron plates constructing special protective devices like safety masks and working with gripping tongs – similar to in the case of working with chloroacetylenes, but in this case with long gripping tongs ecc, all described in **PROJECT XII** and (848) in (2).

We took the opportunity to pass on some of the other experience we made while working with dichloroacetylene, in particular free of and low in ether.

To avoid accidents, we used 1.5 m long grip arms, protective face masks, thick rubber gloves and breast shields and conducted all experiments in the open, not least on account of the toxicity of C_2Cl_2 and its autoxidation products.

Over years, the following incidents occurred with dichloroacetylene, the biggest one in 1960:

a) Luckily, the biggest explosion took place during the lunch break, but *completely destroyed the big apparatus* (Illustration 1) for preparing larger quantities of dichloroacetylene from trichloroethylene (including *stands* and *metal oven*). When we returned, we were surprised that the *whole brick-built construction*, about 4 m in size (Ill 1), that had been located on the flat roof of the old Mannich Institute in Königin-Luise-Straße 2 - 4 in Berlin-Dahlem had *disappeared completely*. Maybe the cause was a leak and / or insufficient flushing with N₂ after a previous attempt to manufacture ether-free dichloroacetylene.

b) On opening a bomb tube that had been filled with a concentrated C₂Cl₂ / CCl₄ solution and heated for a time, the unconverted C₂Cl₂ exploded, blowing the seal on the steel cyclinder up to the ceiling.

c) Approx 15 g low-ether dichloroacetylene that had been produced by stirring a C₂Cl₂ / CCl₄ solution with water and was under water in a seperating funnel, caught fire when the cock was opened, burning the plug.

The rest of the C₂Cl₂ exploded shortly after (the seperating funnel disappeared and the support ring on the stand the funnel had been in was badly twisted).

d) There were several cases of fires and explosions occurring when stirring ether solutions with tap water, trashing the apparatus in one instance.

e) Explosions partially destroyed our apparatus for preparing pure dichloroacetylene by the trichloroethylene method several times, and once completely: the cause was a leak and too weak N₂ dilution.

f) Blow-outs of low-ether dichloroacetylene occurred several times while transferring it to reaction vessels (probably through vortexing in the filling chamber and limited contact with atmospheric oxygen). However, this never caused any serious explosions.

g) upon opening the flask, an approx 58 mol per cent C₂Cl₂ / ether solution, prepared by the trichloroethylene method, self-ignited in rainy weather (extremely damp air) and deflagrated, causing lots of soot. The whole lab smelt intensely of phosgene.

h) O Matter wrote an own report about the "jet engine fuel additive" experiments carried out in Swedish industry profiting from our experiences and advices - regarding also the incidents which occurred there.

SF₆ and Helium (146,1 : 4) were compared: In one experiment we compared the two invisible colorless gases, in second experiment we used both gases dyed.

SF₆ was poured like a liquid in a container, light objects could “swimm” on the surface of this “liquid”.

It could be demonstrated that SF₆ is not inflammable.

We studied in the years between 1941 and 1970 the different methods of SF₆-preparation, its purification and by-products (Table 3) as well the toxicity of pure and not purified SF₆ against mice and rats. SF₆ in 99,9% purity is *nontoxic*.

In a conversation with the famous illusionist Kalanag (who worked together with Gloria) the author found out that Kalanag made also use of this magic gas in his excellent performances that had taken place in the Titania Palace in Berlin in the 50ies. Kalanag was glad to have been informed about the different toxicity of pure and on the non-toxicity of 100% purified SF₆.

To purify SF₆ we used in all cases the method described in Tab 4. A good test to check the purity of SF₆ is the reaction of mice and of new born guppies. SF₆ purissimo is *non toxic* as already mentioned.

SF₆ shows a high stability: Inert gas character (today it is used as isolating gas in industry). SF₆ is completely inpolar.

SF₆ is not attact by OH' , but it is reacting with K and Na in liquid NH₃ , i.e. according to the following equation:

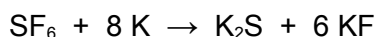
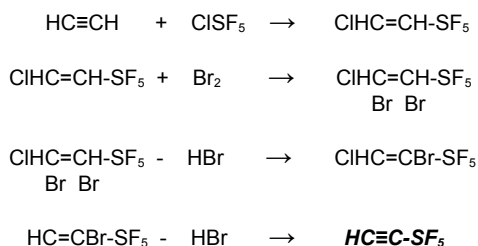


Table 4: SF₆-preparation methods – including purification

nr	principle according to equation	Remarks
I	starting from JSF ₅ $\text{JSF}_5 + \text{HgF}_2 \rightarrow \text{SF}_6 + \text{HgJ}$	1941, working prescription and catalyst from Kautsky,
II	starting from C ₂ JSF ₅ , 1-iodo-2-thiopentafluoro-acetylene $\text{HalC—CSF}_5 + 3 \text{F}_2 \rightarrow \text{SF}_6 + \text{HalF}_2\text{C—CF}_3$	1952, prescription Riemschneider, Stuck.
III	starting from sulfur and fluorine gas (300-400°C) $\text{S}_8 + 24 \text{F}_2 \rightarrow 8 \text{SF}_6$ by-reaction starting from sulfur and less fluorine gas (300-400°C) $\text{S}_8 + 20 \text{F}_2 \rightarrow 4 \text{S}_2\text{F}_{10} \rightarrow 4 \text{SF}_6 + 4 \text{SF}_4$	1966, prescription Riemschneider, Scherer
	Purification of SF ₆ , passing water, alcali (eq), active coal, drying, and followed by pressure destillation to eliminate by-products $\text{SF}_4 + 6 \text{OH}' \rightarrow \text{SO}_3'' + 4 \text{F}' + 3 \text{H}_2\text{O}$	

As mentioned above, SF_6 was prepared in the frame of studying the chemistry of the addition of ClSF_5 to acetylene resulting in chlorothiopenta-fluoroethylene, transforming this ethylene derivative into its (Cl-free) gaseous *parent substance thiopentafluoroacetylene*:



See references (6,7) and PROJ XII 4,2, including unpublished working prescriptions from 1941.

It was possible to replace its hydrogen of thiopentafluoroacetylene by halogens via its Grignard compound, receiving the four 1-halogen-2-thiopenta-fluoro-acetylenes: C_2SF_6 , C_2ClSF_5 , C_2BrSF_5 , and C_2JSF_5 : Table 5

Table 5: 1-Halogen-2-thiopentafluoro-acetylenes

formula _empirical_	halogen in 1 position	mp. °C	bp. °C	mol-weight. found (calc.)		obtained from $\text{HC}\equiv\text{CSF}_5$ and
C_2JSF_5	J	-50	from 65	275	(280)	J_2 (–80°C)
C_2BrSF_5	Br	-64	59	233	(230)	Br_2 (–80°C)
C_2ClSF_5	Cl	-70	45	184	(186)	Cl_2 (–130°C)
C_2SF_6	F		from 30			*)

*) from $\text{JC}\equiv\text{CSF}_5$ and HgF_2 (+ catalyzer)

Summary

- 1) The explosive character of benzotriazole surprisingly found in 1937/39 and chemical experiments with diaminodinitroethylene conducted between 1939 and 1942 drew the author's attention to "*N-rich high energy compounds*" as explosives.**

A list of the N compounds contemplated was submitted or sent, respectively, by the author to the Military High Command in Berlin in December 1942 and the Ministry of Defence in Bonn in 1956; list in accordance with Plate 1a and 1b: I to XI and Formula Summary A.

The cited compounds and, in some cases, their picrates, nitrates and azides were synthesised by the author and his colleagues and tested for explosive action and compared with TNT in cooperation with the engineer O. Matter of Vitznau, Switzerland: Heat of explosion and detonation (P,D), stability, heat, friction, electrostatics. Highly positive results in some cases (restricted access). Continued in Brazil.

- 2) In serial experiments with the nitration of *m*-dinitrobenzene to obtain the *s*-trinitrobenzene, it was noted that partial degradation to tetranitromethane occurs; conception of a method of analysis for determining the three nitration products; analogously, experiments in the direction of trinitroanisol.**
- 3) At the request of the Ministry of Defence in Bonn, the author conducted systematic studies on the *permeation behaviour of the warfare agent LOST and the nerve gases Tabun, Sarin, etc. vis-à-vis polymers of all kinds* over more than 10 years (topic: protective gear). Result in 1957: Teflon is the best possible solution. This material virtually "protects" linen, cotton, wool, silk, leather, blends - all kinds of fabrics.**

References:

- (1) R.Riemschneider
Bonded to people
<http://www.bwwsociety.org/journal/html/bondedtopeople.htm> 2008

- (2) R.Riemschneider
"Re-reading 66 Years Chemistry" with approx. 1500 citations (own publications, lectures, lab.reports, patents), PROJECT I and XII (in preparation)

- (3) R Riemschneider
"Chemical warfare agents" („*Chemische Kampfstoffe*")
Lecture II given to staff officers in lecture hall of (German) Army High Command in Jebenstraße, Berlin on 21 Dec 42, chair: Major Kassuba.
Ms 16 p + 10 slides; cf SPECIAL PART B.

- (4) R Riemschneider
"Chemical propellants for rockets" („*Chemische Treibmittel für Raketen*")
Lecture I given to staff officers in lecture hall of (German) Army High Command (OKH) in Jebenstraße, Berlin on 20 Dec 42, chair: Major Kassuba.
Ms 14 p + 12 slides, completed later into lecture in Dec 56, given in Vitznau; cf SPECIAL PART C
Both lectures (3, 4) were given at the orders of (German) Army High Command in the frame of the author's interview for his future position at the (German) Army Explosives and Warfare Agents Research Establishment in Prague (from Jan 43).
The author was able to prepare these lectures (819 a, b) during a stay in the military hospital at Furth im Wald. The literature was obtained with the help of Prof Dr J Goubeau of Göttingen and the material for the slides by the hospital's secretariat. The slides were prepared by the Army High Command and had to remain there with the original lecture scripts.

- (5a) R Riemschneider , K.Brendel
Preparing and handling dichloroacetylene
Liebig's Ann Chem 640, 1-13 (1961)

- (5b) R Riemschneider
„Comparison the properties of C_2Cl_2 and C_5Cl_6 ”
 C_5Cl_6 is not qualified as explosive.

- (6a) C Weygand, H Kautsky, R Riemschneider
"Chlorinating" acetylene with $CISF_5$ ¹ resulting in chlorothio-pentafluoroethylene from bp 66 – 67°C (I) („*Chlorierung*" von Acetylen mit $CISF_5$:
Chlorthiopentafluorethylen vom Sdp. 66 – 67°C)
Lab report I, May 41, 7 p (secreted)
Experiments conducted in Dept of Org Chem (head: Prof Dr C Weygand) Inst of Chem, Univ of Leipzig.
The report contains the instructions for obtaining $CISF_5$ and converting this sulfohexaheterohalide with acetylene also instructions for obtaining SF_6 from $CISF_5$; protocol to maintain secrecy signed.
Details in SPECIAL PART XII 4.2
100 g of the chlorothiopentafluoroethylene (I) prepared in Apr 41 were sent with the agreement of Kautsky by courier attn Dipl Chem R Riemschneider at the (German) Army Explosives and Warfare Agents Research Establishment in Prague to be tested for suitability as a warfare agent: Tab 1, pt 4

¹ This sulfohexaheterohalide was first prepared by Prof Dr H Kautsky, Head of Dept of Anorg Chem, Univ of Leipzig

- (6b) H Kautsky, R Riemschneider, C Weygand
Acetylene sulfopentafluoride from chlorothiopentafluoroethylene (*Acetylen-schwefelpentafluorid aus Chlorthiopentafluorethylen*)
Lab report II, May 41, 8 p (secreted) classified as important to the war effort; cf XII 4.2.
Experiments conducted in Dept of Anorg Chem, Inst of Chem, Univ of Leipzig; cf XII 4.2
Ibidem, also prepared SF₆, an "invisible" high-density gas, according to Kautsky suited for "magic experiments" that depend on "invisible heaviness"; cf (817d).
SPECIAL PART F of internet publication; issued in 2009 at:
<http://www.bwvsociety.org/journal/html/explosives.htm>
- (7) R Riemschneider, H Blunck, H Remy
"Chlorinating" acetylenes with chloromethylthiochloride to C₄H₄S₂Cl₄ bp 41 – 43°C (12 torr) („Chlorierung“ von Acetylen mit Chlormethylschwefelchlorid zum C₄H₄S₂Cl₄ vom Sdp. 41 – 43°C)
Lab report, Nov 40, experiments conducted in Dept of Anorg Chem, State Chem Inst, Univ of Hamburg, Jungiusstraße.
cf PROJ IV [(357 a - e, 358) in (2)]; ibidem working instructions (357 d)
Substituting H atoms of acetylene with hypochlorite at (812 a) and later refs, above all (821 a, 848, 850 b);
cf PROJ XII 4.1 [(833) in (2)] on converting acetylene with SeCl₄
- (8) R Riemschneider, C Weygand, A Suhr
C₄N₂S₂Na₂ from "CS₂ + NaCN", likewise intended as a "nitrile group donor" (C₄N₂S₂Na₂ aus „CS₂ + NaCN“, ebenfalls gedacht als „Nitrilgruppen-Spender“)
Experimental protocol of Sept 38, 6 p; cf XII 4.4.1.
This protocol, as well as the experiments of Oct and Nov 38 [(812a,b) in (2)], was part of the author's handwritten final year's work in chemistry at college, submitted at the Matthius Claudius High School in Hamburg-Wandsbek in Jan 39. In all the work covered experiments from Oct 37 to Dec 38, totalling 96 pages; cf PROJECT I, there ref (1) in (2).
"CS₂ + NaCN" forms a salt with the empirical formula C₄N₂S₂Na₂ (Eq 12 in XII 4.4.1), methylated to C₆H₆N₂S₂ (Eq 13 in XII 4.4.1)
- (9a) R. Riemschneider
Silanes
<http://www.bwvsociety.org/journal/html/silanes.htm> **2007**
- (9b) R. Riemschneider, F.R. Pessler, F. Herzel
Synthesis of Silanes, Si_xH_{2x+2}, and **Polysilanes**, (SiH₂)_x
3 lab reports 1987, 19 p (proposed to HOECHST and secreted).
Content: Halogenated silanes can be reduced to silanes better with LiAlH₄ than with Na. Perhalogenated silanes, (SiCl₂)_x [prepared from SiCl₄ + H₂] deliver under these conditions (SiH₂)_x :
(SiH₂)_x is a solid powder, O₂-sensitive, to be stored under N₂ ; from 70° C on self-igniting, under N₂ at 275° C decomposition into H₂ + SiO₂ (not melting), in dil NaOH delivering H₂ + SiO₂ , that means (SiH₂)_x promises to become an interesting "Hydrogen-carrier" : SiO₂ → SiCl₄ + H₂ → (SiCl₂)_x → (SiH₂)_x . Si itself can also serve as an "Hydrogen-carrier" [Si + H₂O + 2NaOH → 2H₂ + Na₂SiO₃], but less effective than (SiH₂)_x, from Labs of BRASTONE and CONCLUTING DEVELOPMENT ENGINEERING, Curitiba and S. Paulo, and from the Central Inst of Chemistry, UFSM, S. Maria, Brazil; cf. (9a) there ref [14].
- (10) R Riemschneider, R Souza, F R Pessler, C Brandmayer

P-F bond-cleaving enzymes as antidotes for use against neurotoxic warfare agents
- isolation and application (*P-F-Bindungen spaltende Enzyme als Antidote zum Einsatz gegen Nervengift-Kampfstoffe - Isolierung und Anwendung*)

Four secreted lab reports from 1949 - 62

A co-worker, Dipl Chem G Koh, established contact with AUER Co and via it with the Ministry of Defence (above all via Prof Dr Lendle, pharmacologist at the Univ of Göttingen).

Experiments started in AUER labs, later in Berlin; cf. PROJ XVIII in (2).

(11) R. Riemschneider

Trinitroanisol – preparation (series of tests) and properties.

3 Lab reports 1943/44, 14 p (secreted)

Experiments conducted like (13c) and later in the Physiolog. Chem. Inst., Univ. Berlin (unpublished)

(12a) R.Riemschneider , A.Kühnl

Verification of information that some plants such as mosses produce ammonium nitrate.

First lab report dated February 1943 from the Institute of Explosives in Prague; experiments continued at the Free University in Berlin from 1955 onwards.

Positive results indicate that the mosses which, having no roots, draw their nourishment from the surrounding air withdraw N compounds from said air and convert them to nitrate: Opportunities for keeping the air clean or purifying it (?).

Ammoniumnitrat (responsible for the OPPAU incident September 1921) had inspired the author to look for energy carrier not only under Nitro- but also under N-rich compounds: Formula Summary A.

The apartment of the author's parents in 1921 was nearby Ludwigshafen-Oppau; so they told him later that he noticed the "Explosionsdruckwelle" (window glass splitting) crying loudly in his age of one year. Der Explosionsknall soll bis in das 80km entfernte Frankfurt/Main zu hören gewesen sein.

(12b) R.Riemschneider

Nachweis von Tetranitromethan in Produkten der Nitrierung von m-Dinitrobenzol mit rauch. HNO_3 + rauch. H_2SO_4 .

Laboratory report 10 Febr 1943, 6 p (secreted)

Experiments from (German) Army Research Establishment for Explosives in Prague

(12c) R.Riemschneider, A. Kühnl

Ausarbeitung einer polarographischen Methode zur quantitativen Bestimmungen von 1,3,5-Trinitro-benzol neben m-Dinitrobenzol und Tetranitromethan (Modellversuche).

Ms 27 Febr 1943, 10 p (secreted),

handed to Dr K Cruse, head of section, on 28 Febr 1943 in Prague in presence of Dipl Ing A Kühnl. K. Cruse and H.Haul published in 1949 a paper that had been based completely on the data given in Section II 1 b) of this essay (i.e.on this reference) - **without any hint to the origine**; they did not explain that and why these experiments were done by the author in the German Army Research Establishment for Explosives and Warfare Agents in Prag at the beginning of 1943. Ing A.Kühnl, working also in this institution, had written an affidavit in 1950 confirming these events.

Der oben genannte Aufsatz ist von Cruse und Haul in der "Zeitschrift für Elektrochemie" veröffentlicht worden. Verfasser hat per Einschreiben 1949 der Reaktion die Wahrheit über die veröffentlichten Ergebnisse mitgeteilt und zum Beweis Unterlagen über seine Versuche aus dem Jahre 1943 beigelegt, und zwar: ca. 20 Polarogramme, Berechnungen über die Reduktionspotentiale bei den pH-Werten 5,0 bis 13,5 - einschliesslich der praktischen Anwendung der Methode.

Kopie an Professor Dr.G.Rienäcker, Universität Rostock. Ferner hat Verfasser ausführlich im Einschreiben dargelegt, warum er die Methode der Bestimmung der Nitroverbindungen entwickelt hat, und zwar um in Reihenversuchen die Ausbeute an Trinitrobenzol zu verbessern. Im Rahmen solcher, in Gegenwart von Dipl.Ing.A. Kühnl und zeitweise auch mit F.Maaz, durchgeführten Untersuchungen ist auch entdeckt worden, dass Tetranitromethan bei zu scharfen Nitrierungen als Abbauprodukt entsteht. Es handelte sich hier um reine organische Chemie, mit der Cruse und Haul nicht vertraut waren.

- (12d) R.Riemschneider, A.Kühnl
Nitrierung von m-Dinitrobenzol zu Trinitrobenzol¹
2 Laboratory reports of 19 Febr 1943 and 18 March 1943, 26 p (secreted)
Preliminary tests and series of tests to establish the optimal experimental conditions and reduce the side reactions like formation of tetranitromethane etc. See text for criticism of conducting such tests in 1943². *Tests conducted protected behind iron plates and working with gripping tongs – similar to in the case of working with di- and monochloro-acetylene: SPECIAL PART E*
"Kindly make these experiments without me," said Kühnl, who was the author's senior by 20 years, in his soft Austrian dialect. "I have a family, and we have no chance of winning this war anyway." The author would like to emphasise that he considered this associate a friend whose technical qualification was much appreciated. Our friendship of 20 years lasted until Kühnl's death.
- (12e) R.Riemschneider
Lecture I: „Literatur zur Analytik von m-Dinitrobenzol, 1,3,5-Trinitro-benzol, Tetranitromethan und über die Versuchsergebnisse zur Einführung einer dritten Nitrogruppe ins Dinitrobenzol“ given on 28 March 1943 in chemical colloquium of (German) Army Research Establishment for Explosives, Prague: Final report on results achieved at (13a-e) in connection with literature studies.
- (12f) R.Riemschneider
Lecture II of 28 March 1943: „Anwendung der polargraphischen Bestimmung von Dinitrobenzol, Trinitrobenzol und Tetranitromethan auf Reaktionsgemische der m-Dinitrobenzol-Nitrierungen (mit rauch. HNO₃ + rauch. H₂SO₄)“
Experiments conducted in (German) Army Research Establishment for Explosives, Prague in Febr and March 1943
Ms March 1943, 11 p; cf also (13b) and PROJ V 4.1
- (12g) R.Riemschneider, A.Suhr, F.Faltings
Über das polarographische Verhalten einiger Halogenkohlenwasserstoffe (Studium der HEYROVSKI-Methode)
Lab report Juni 1940, task „Pratikum der Physikalischen Chemie“ under Prof Harteck.
- (12h) O.Matter, R.Riemschneider, C.Brandmayer
Acylation of 1,1-diamino-2,2-dinitro-ethylene (**XI**) with *oxalyl chloride* to 2-dinitromethylene-imidazolidine-4,5-dione (**XII**), with *propionylbromide* to monopropionyl-**XI** : *Formula Summary F* (in PROJ I 2, point 12, further investigation),
Lab report 1947 and 1954, 10p (secreted).
Ing O.Matter, a friend of the author³, co-operated with a Swedish company in matter explosives and received the task to investigate the reactivity of **XI** and to

¹ see also PROJECT V 4.1 in (2)

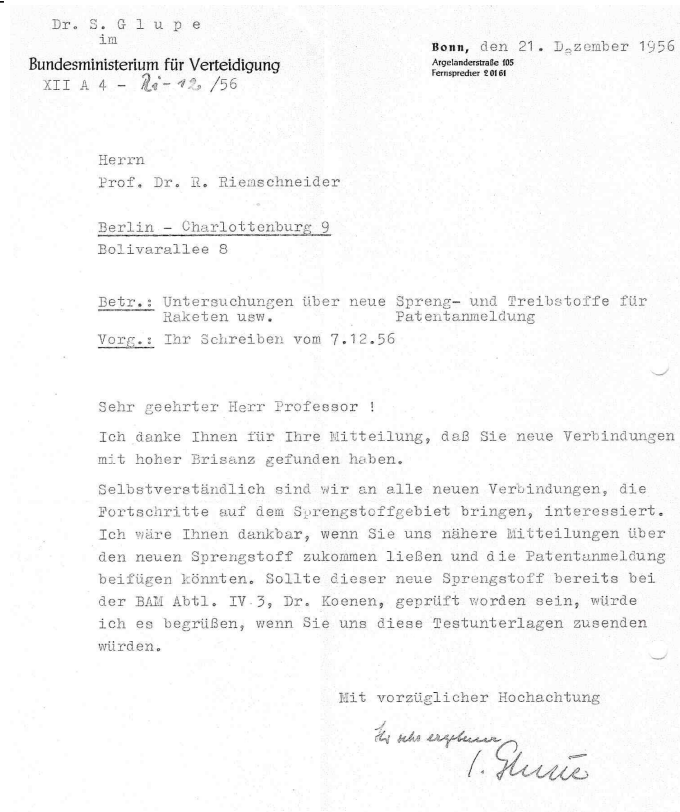
² Unfortunately no contact whatsoever with Peenemünde (or Hitler-Tunnel) where they were already working on rocket fuels. After the destruction of the Peenemünde installations in 1943 all rocket research and the production of V1 and V2 weapons took place underground in the so-called Hitler-Tunnel.

³ cf "Bonded to People" at 4a) Matter , and Special Part K)
<http://www.bwvsociety.org/journal/html/bondedtopeople.htm> 2008

look for a simpler **XI**-synthesis. 25g **XI** had been at our disposal from the Swedish company.

Formula Summary A sent to the “Bundesministerium für Verteidigung” in Bonn. Confirmation of receipt in Plate 12.

Plate 12:



- (12i) R.Riemschneider , H.Doll
1,2,3-Benzotriazol – explosiv
Laborbericht , Dezember 1939

When the author attempted to rectify the 1,2,3-benzotriazole he had prepared by vacuum distillation, a severe explosion occurred. The author resolved to consult literature (Chemical Abstracts) in order to find out what was known about the explosiveness of compounds rich in N (triazoles, tetrazoles, pentazoles, NH₂ derivatives thereof, picrate salts, etc.).

The 1,2,3-benzotriazole explosion observed and the above-mentioned literature consultation later on resulted in planning the Formula Summary A Plate 1b).

- (12j) R. Riemschneider, A. Kühnl, H. Schmidt, F. Scherer
Synthesis and explosive characteristics of 1,2,3-benzotriazole mp 98-99°C (*Synthese und Explosionscharakter des 1,2,3-Benzotriazols vom Schmp. 98 – 99°C*), 1st lab report from 1943 (Prague), 2nd 1949, 6 p (unpublished)
Together with Dipl Eng A Kühnl, author synthesized this compound in the (German) Army Explosives Research Establishment in Prague in 1943 um eine Wiederholung des Versuches vorzunehmen.

The compound showed growth effects on plants during later experimental tests in Farbwerke HOECHST's Crop Protection Department (1950); cf. 3rd lab report (with the director, Dr F Scherer), 1951, 8 pages (secreted)

- (12k) R.Riemschneider, D.Kirstein, R.Patel, M.Azhar
2,4,6-Trinitro-anisol – preparation and its polarographic determination
Lab report 1975, Chemical Central Institute of UFSM, S.Maria, RS, Brazil
- (12L) R.Riemschneider
Stand der Ergebnisse der Permeationsversuche „Polymere/LOST, TABUN, SARIN“ – Bericht II (1958):
Teflon (Tetrafluorethylen-Polymerisat) zeigt die besten Ergebnisse hinsichtlich Widerstandsfähigkeit gegenüber LOST und Nervengasen. Teflon ist ausserordentlich inert, praktisch unlöslich, thermisch verformbar (Temperaturbereich von -150°C bis $+250^{\circ}\text{C}$). Anzüge mit Teflon beschichtbar (diese Versuche von W.Schneider). Interner Bericht [gemäss Abkommen für immer sekretiert].

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