②

FRAUNHOFER-INSTITUT
FÜR TREIB- UND EXPLOSIVSTOFFE

PROCESS FOR ASSESSING THE STABILITY OF HAN-BASED LIQUID PROPELLANTS

3rd Interim Report

by

Dr. R. Hansen
Dr. E. Backof
Dr. H. J. de Greiff

December 9, 1987

United States Army

EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY

London England

CONTRACT NUMBER DAJA 45-86-C-0056

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

7507 PFINZTAL-BERGHAUSEN
BEI KARLSRUHE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
3 rd Interim Report

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Process for Assessing the Stability of HAN-Based Liquid Propellants

5. TYPE OF REPORT & PERIOD COVERED
Interim Report
9th June 87-9th Dec. 87

6. PERFORMING ORG. REPORT NUMBER
19 / 101 664

7. AUTHOR(s)
Dr. R. Hansen
Dr. E. Backof
Dr. H. J. de Greiff

8. CONTRACT OR GRANT NUMBER(s)
DAJA 45-86-C-0056

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Fraunhofer-Institut für Treib- und Explosivstoffe
(ICT), Joseph-von-Fraunhofer-Straße,
D-7507 Pfinztal-Berghausen (F.R.G.)

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Task Description 4.2
Work schedule 2.2., 3.1.1

11. CONTROLLING OFFICE NAME AND ADDRESS
Fraunhofer-Gesellschaft
Leonrodtstr. 54 , 8000 München, F.R.G.

12. REPORT DATE
December, 9th, 1987

13. NUMBER OF PAGES
30

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
Bundesministerium der Verteidigung der
Bundesrepublik Deutschland (MOD)
5300 Bonn, F.R.G.

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

~~To be decided by the USA ECA~~

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Liquid Propellants, Monergols (HAN-based), Long Term Stability,
Decomposition time, life term

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The third Interim Report, Part I, describes the testing and selection of metallic and non-metallic materials for application in pressure-testing apparatus to determine the life term of HAN-based liquid propellants (LPs). Metallic materials are necessary for pressure sensors and non-metallic materials for sealing of the testing apparatus. Selection criteria for the metals are their corrosion-resisting quality and their capacity to influence or restrict the chemical stability of the LP. Selection criteria for the sealing materials are their impermeability to gases, deformation under strain and compatibility with

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

continuation on reverse side

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) contd → 20. Abstract (continued)

the LP used. The testing apparatus is being used at the present time. Testing results will be discussed in the next Interim Report.

The 2nd Part of the present Report will describe the experiments carried out on the long-term storage of LP 1846 in glass ampoules at 90 °C (194 °F): metal-ions at different concentrations, i.e. 100, 10, 5 and 2 ppm, are here added to the propellant. The time up to the bursting of the glass ampoules (i.e. the respective storage capacity) is measured. In addition to iron and copper ions, vanadium and palladium ions greatly reduce the life term of the liquid propellants tested. In comparison to the original propellant, however, the metal ions of tungsten, zirconium, chromium and manganese exert no influence on the storage life of the LP. We were not yet able to find a stabilizing influence of complex-forming substances on contaminated LP samples.

→ (Keywords:)

FRAUNHOFER-INSTITUT
FÜR TREIB- UND EXPLOSIVSTOFFE

PROCESS FOR ASSESSING THE STABILITY OF HAN-BASED LIQUID PROPELLANTS

3rd Interim Report

by

Dr. R. Hansen
Dr. E. Backof
Dr. H. J. de Greiff

December 9, 1987

United States Army

EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY

London England

CONTRACT NUMBER DAJA 45-86-C-0056

7507 PFINZTAL - BERGHAUSEN
BEI KARLSRUHE

List of Contents

1. Abstract

The Third Interim Report, Part 1, describes the testing and selection of metallic and non-metallic materials for application in pressure-testing apparatus to determine the life term of HAN-based liquid propellants (LPs). Metallic materials are necessary for pressure sensors and non-metallic materials for sealing of the testing apparatus. Selection criteria for the metals are their corrosion-resisting quality and their capacity to influence or restrict the chemical stability of the LP. Selection criteria for the sealing materials are their impermeability to gases, deformation under strain and compatibility with the LP used. The testing apparatus is being used at the present time. Testing results will be discussed in the next Interim Report.

The 2nd Part of the present Report will describe the trials carried out on the long-term storage of LP 1846 in glass ampoules at 90 °C (194 °F). Metal ions at different concentrations, i.e. 100, 10, 5 and 2 ppm, are here added to the propellant. The time up to the bursting of the glass ampoules (i.e. the respective storage capacity) is measured. In addition to iron and copper ions, vanadium and palladium ions greatly reduce the life time of the liquid propellants tested. In comparison to the original propellant, however, the metal ions of tungsten, zirconium, chromium and manganese exert no influence on the storage life of the LP. We were not yet able to find a stabilizing influence of complex-forming substances on contaminated LP samples.

2. The influence of metallic and non-metallic materials on the chemical stability of LP 1846

In measuring the pressure rise in liquid HAN propellants at increased temperatures during long-term storage, it is first of all necessary to make sure that material components of the pressure sensors and the sealing elements exert no influence on the life term of propellant samples. We consequently first tested the interactions between metals, alloys and sealing materials on LP 1846.

2.1 Metals and alloys

The accelerated storage tests were continued on the effects of precious metals, metals, stainless steels and gun steels on LP 1846 in glass ampoules, thus expanding on Table 4 of the First Interim Report. We measured the time up to bursting of the ampoules.

The decomposition times of LP 1846 at 90 °C (194 °F) under the influence of metals and the relative life term are listed in Table 1 (of this Report). The metals were added in the form of filings or powder and not as compounds, such as e.g. salts. The relative life term is given as a percentage of the original LP 1846, the life term of the original being fixed at 100 %. Changes in the LP or the metallic additives are recorded in Column 4 of Table 1.

Of the precious metals tested, gold, silver and mercury showed no restriction in the life term of LP 1846.

Some of the metals used as alloying components enter into solution in LP 1846, forming metal complexes. In spite of the chemical reactions involved, the time up to the bursting of the ampoules can be equal to that of the original sample or even be longer. These time periods are equal in the case of zinc, and that of manganese longer by 10 %. Both lead and aluminum, which are not quantitatively dissolved in LP 1846, also increase the storage duration of the propellant. The cause for this lies in the fact that condensed reaction products, formed from the metals and the liquid propellant, delay or slow down the development of gaseous decomposition products.

The majority of added metals shorten the storage duration of LP 1846 considerably, some of them (such as iron, copper and antimony) by more than 90 % to < 6 %.

The stainless steels tested also produce a considerable shortening in the storage life of the liquid propellant. Thus, the storage life of LP 1846 is reduced by 26 % to 74 % when in contact with Stainless Steel, Standard No. 1.4571, and by as much as 97 % to 3 % with Stainless Steel, Standard No. 1.4541. At 90 °C, material 17/4 PH (No. 1.4542), which is used in making the pressure sensors, shortens the storage life of the propellant by 77 % to 23 %.

Under the condition described (90 °C), the two gun steels, Standard No. 1.6580 and No. 1.2760, already decompose the liquid propellant within a single day.

Attempts to passivate stainless steels against LP 1846 were not carried out at the ICT. Practical experience in this field was, however, made at the BRL /1/.

Long-term storage tests on LP 1846 when in contact with metallic materials (Table 1) have shown that gold causes no reduction at all in the storage life of the propellant. Consequently, the pressure sensors, made of construction material 17/4 PH were galvanically gold-plated. Preliminary coating was with Au/Co, the second coat was of pure gold. The gold plating had a thickness of approx. 40 µm. After this process, each sensor was tested for pore sealing. In order to protect the parts not intended for gold plating, 30 cm long radiated cross-linked shrinking PVC tubes were drawn over the pressure sensors and their connecting cables during the galvanization process and subsequently removed.

2.2 Plastomers and elastomers

The materials for sealing the pressure sensors must be selected with the same care as those for the pressure sensors themselves.

The demands made on the sealing materials are:

- High chemical resistance to the liquid propellants (both in the liquid and gas spaces) as well as to the decomposition products of the LPs,

- No influence on the sealing materials used to the chemical stability and storage life term of the liquid propellants.

For the selection of suitable sealing materials, a total of 9 different plastomers and elastomers, listed and described in Table 2, were stored in glass ampoules in the liquid phase and in the gas space of LP 1846 at 90 °C (194 °F). The time measured up to the bursting of the ampoules is a parameter for the storage life of the propellants under the influence of the sealing materials.

The storage life of the propellant/sealing sample is compared with the storage life of the pure propellant (100 %). The results are compared in Table 3.

The tests showed that only Teflon (PTFE-PT950; PTFE-TFM), PFA and polytrifluorochloroethylene (PCTFE) are here applicable. The decomposition time of these substances reaches that of the original LPs.

3. The physical properties of sealing materials

Apart from their chemical stability as well as their compatibility with the liquid propellant, selection criteria for materials used in sealing glass pressure containers also include their permeability to gases and their viscous flow behavior.

3.1 The permeation of gases through high-polymer substances

All plastics are more or less permeable to gases. Taking a layer made of plastic with a thickness d and surface A (example: planer membrane), a pressure difference Δp between the two sides of a membrane causes a gas flow Q from one side to the other. This transport process is called 'permeation'. If Δp is not too high, this permeation process may be described by the linear relation:

$$Q = P \frac{A}{d} \cdot \Delta p$$

P is a constant and is termed 'permeability' or 'permeation coefficient'. The above quantity P depends on the nature of the gas/membrane system and on the temperature. P is an exponential function of the temperature.

$$P = P_0 \exp(-E/RT),$$

in which E is the activation energy, R the gas constant, T the temperature in degrees Kelvin, and P_0 a constant. When ln P is plotted versus 1/T, the equation produces a straight line. For the calculation of P as a function of T, this diagram can be used e.g. for extrapolations.

The SI units of the quantities therefore important for our calculations can be found in the following list:

Quantity	Q	A	d	Δp	T	P
Unit	$m^3 \cdot s^{-1}$	m^2	m	Pa	K	$m^2 \cdot s^{-1} \cdot Pa^{-1}$

The gas volume in quantity Q is converted to standard temperature and pressure conditions (1.013 bar, 0°C, i.e. = NTP). Other, incoherent units are often also used in practice, so that a conversion must be undertaken for reference purposes.

Permeation coefficients depending on temperature for a number of gases and sintered PTFE (the product 'Hostaflon' as manufactured by Hoechst AG, FR Germany) have been placed together for comparison in Tables 4 and 5. The manufacturer gives the permeation coefficient for a layer thickness of 1 mm in $cm^3/day \cdot m^2 \cdot bar$.

The temperature dependency of the permeation coefficients for amorphous PCTFE ('Voltalef' as manufactured by the ATOCHEM Co., FR Germany) are listed in Table 6. Fig 1 shows the exponential dependence of permeability from temperature.

From permeability coefficients given by German manufacturers, gas fluxes were calculated for the flat sealing materials of the glass vessels used in the pressure-testing apparatus. In order to calculate the effective surface A of the ring-shaped sealing elements (r_o = 6 mm; r_i = 4mm; h = 2 mm), a mean radius of r_m = 5 mm was used for the purpose of simplification:

$$F = 2\pi\ r_m h = 0.63\ cm^2;$$

$$d = r_o - r_i = 2\ mm.$$

For sealing elements made of PTFE and PCTFE with these dimensions, the permeating gas fluxes were calculated in cm^3/day for temperatures from 25 to 90 °C (77 to 194 °F): these values are given in Table 7. Calculation is based on the permeability coefficients converted according to Fig. 1 as given in Tables 4, and 6.

It can be seen from Table 7 that - in one and the same material - the gas fluxes Q are heavily dependent on the permeating gas: carbon dioxide permeates approximately 10 times more rapidly than nitrogen (in TF 1740 and TFM 1700); in Voltalef 300, there is a factor of about 30. The gas fluxes Q or, correspondingly, the permeation coefficients P increase considerably with temperature in all cases; the differences between the two PTFE types (manuf. Hoechst) are, however, slight.

The modified Teflon TFM has a permeability lower than that of TF 1740 by the factor of 1.5. Great differences exist between PTFE and PCTFE. At 25 °C (77 °F), the permeability of PCTFE is lower than that of TFM by a factor of 60. The temperature dependency of the permeabilities between PTFE and PCTFE cannot be compared as only measurement results with helium are available for Teflon. In the case of nitrogen, the permeability of Voltalef 300 increases by a factor of 39 from 25 °C to 90 °C (77 °F to 194 °F); these factors are 27 for oxygen and 19 for carbon dioxide.

As the propellant samples are stored at 90 °C (194 °F), the gas leakage must also be known for this same temperature. Where PCTFE is concerned, this is within a range of 1.10^{-2} cm^3/day at a pressure difference of 5 bar. Storage experiments are discontinued at 5 bar. In the original samples of 1846, this terminal pressure is only reached after approximately 70 days. Initially, the pressure curves progress in a very flat form to rise exponentially shortly before the end of the experiment.

If we assume that, over a test period of 100 days, a pressure of 5 bar is present at the surface of the flat sealing material, the gas loss then amounts to approx. 1 cm^3. The testing apparatus has a volume of 2 cm^3. At a pressure of 5 bar, this corresponds to approx. 10 ml gas under standard conditions. A loss of 1 cm^3 would mean an error of 10 %. As the pressure in the testing apparatus rises slowly and only reaches 5 bar toward the end of the test, the real error is considerably less than that calculated. Nevertheless this error assessment shows that the pressure curves flatten out somewhat toward the end of the test. However, as this is more or less the case with all pressure curves involved, the error equals itself out - this is because the pressure measurements to determine the life term of the liquid propellant do not represent the absolute pressure of the individual samples; instead, the comparitive pressures between the individual samples are here substantial.

3.2 Elasticity and plasticity

Elastomers are specially suited for sealing the glass containers used. The chemical stability and sealing capacity of these materials are prerequirements for their use in long-term tests (100 days at 90 °C/194 °F).

We were not able to obtain warranties from the various manufacturers that their products could maintain these extreme conditions. Initially, we considered making use of Teflon-coated Viton-O rings to seal the storage containers. This Teflon coating has a thickness of 0.4 mm. It can be seen from Section 3.1 that the use of 0.4 mm thick Teflon foil to seal glass containers in long-term tests is not possible due to a too high permeability to gases.

Plastomers, especially Teflon, are subject to deformation under strain. Modified Teflon has 40 % less deformation than the non-modified form. This deformation is even less in the case of PCTFE. Deformation decreases under strain as hardness increases:

The mechanical properties of PTFE AND PCTFE:

Properties	PTFE		PFA	PCTFE
	TF 1740	TFM 1700		Voltalef 300
Deformation under strain (7 MPa-24h/25°C)	2.5 %	1.5 %	-	1 %
Shore hardness	c. 55	60	64	77 - 79

On account of long-term stress of the sealing materials during storage of the LP samples at 90 °C (194 °F), PCTFE was thus selected as sealing material for storage of propellants in measuring the increase in pressure.

In comparison with TFM and PFA, PCTFE has the highest shore hardness, the lowest deformation under strain and the smallest permeation coefficient.

The measuring apparatus was thus fitted out with flat PCTFE sealing units (12 x 8 x 2 mm).

With the test design as described, we hope to be in the position of providing a contribution to determining the chemical stability of liquid propellants and on the influencing of stabiliziers for the storage life of liquid propellants. Initial trials have been started. Results will be communicated.

4. The influence of metal ions on the chemical stability of LP 1846

All HAN-based LPs react to specific impurities with decomposition of the HAN components. There are negative effects on the storage, manipulation and performance of the LP as a result of this decomposition process. Impurities in the propellant result in gas formation in the storage tank: if this is not monitored during storage and transport, a high pressure is then built up as a consequence. Manipulation is thus difficult due to decomposition hazard.

The partial loss of a high-energy component produces an unfavorable change in both the burning behavior and performance of the LP concerned.

Furthermore, the pH value drops due to decomposition and ammonium nitrate is produced as a by-product: this can crystallize out during manipulation under cold conditions /1/. This can result in a constriction and obstruction where sensitive stages are encountered in relevant supply systems. When storing LP 1846 at a temperature of -80 °C (176 °F) over several days, we found that not only those LPs containing ammonium nitrate (0.1 %; 3 %; 5 %; 10 % AN) but also the original samples deposited crystals.

When a free acid is present, we observed an increased instability of the HAN-containing propellant. This dependence on pH can be demonstrated with the help of DSC measurements with NOS-365 (Fig. 2) as example. Where the LPs had been dehydrated in a careful manner, a partial disintegration was already found at 70 °C (158 °F) in the highly acid samples. A production of heat can already be observed at 50 °C (122 °F). The generation of a slight amount of heat can be viewed as being preliminary to a spontaneous decomposition. With a reduction in the concentration of free acid, the peak (Tp) of the decomposition temperature is increased from 70 °C/158 °F (pH = 0.01) up to 187 °C/368.6 °F (pH 1.9). Acid concentrations between these two values are also effective (Fig. 2). The decomposition of IPAN is not shown in Fig. 2, which only shows a section. IPAN does not start decomposing until values greater than 200 °C (392 °F) are reached. An influence of NH_4NO_3 impurities cannot be demonstrated.

This Interim Report provides information on what metal ions are responsible for a decomposition of HAN and at what concentrations. Not until these results are known can a prerequirement for effective influencing action on the stabilization process be established.

4.1. Determining the instability of contaminated LP 1846 using glass ampoules

Testing chemical influences on LP samples was carried out along the lines of a relative method. To simulate aging processes, the prepared LP samples are sealed (i.e. by melting) into glass ampoules and stored at a raised temperature of 90 °C (194 °F). The time up to the bursting of an ampoule is taken as a parameter for the stability of its content. For storage of this type, the same quantities of LP are used at all times, as the decomposition pressure depends on the quantity of HAN used. The metal compounds are - where possible - applied in the form of nitrates, although the oxides had to be used in a number of compounds. The use of nitrates is to exclude a possible influence from anions. In order to avoid an additional strain on the metal ion - HAN redox system, the lowest valency or the most stable ion form was selected in application of the metal ions.

Tables 8 and 9 provide a comparison of the data obtained from tests in ampoules enclosing metal ion additives in concentrations of 10 ppm and 100 ppm. Table 10 gives a comparison of the relative decomposition times. The test data are listed for the highest concentration (100 ppm) after recording of the relative life term.

In the upper section of Tab. 10 those ions are given which exert no influence on HAN decomposition at 100 ppm. The lower part of the table gives the ions which exert the greatest influence on decomposition, and from which the limit concentrations for their efficacy could be determined. In these ions, a high dependency on the concentration is present.

4.2 Experiments on improving the stability of contaminated LP 1846

In conventional solid gun propellants on a nitrate basis, the addition of stabilizers slows decomposition down. It is the aim of adding such stabilizing substances in order to bind nitrous gases chemically. Very weak bases, such as amino and urea (carbamide) derivates, have been found most expedient as additives for solid propellants.

Propellants containing HAN react immediately with nitrous gases: however, these gases react more rapidly with HAN than with the stabilizers for solid propellants. The addition of such 'stabilizers' is therefore not capable of producing any really notable stabilization in liquid propellants containing HAN. Although no mean number of trials have been carried out to test urea derivates and substances reacting in a similar way under this aspect /3/4/, the measurement effects of an improved stability are most probably based on other causes.

As the cause for HAN decomposition is based on the catalytic effects of a definite number of metal ions, new paths must be taken as regards optimizing the stability of LPs containing HAN.

It is the initial aim of all HAN manufacturers to prevent decomposition by avoiding metal ions. Such a demand can only be realized with difficulty when operating with HAN under practical or near-practical conditions. Therefore, the effects of metal ions on the HAN must be elimited through the presence of stabilizers in order to obtain a protective or buffer effect.

A number of different methods have been proposed to solve these problems, i.e.:

The transfer of metal ions into very stable complexes /5/. However, in practice, this is restricted due to the fact that most complex compounds do not possess a sufficient stability in the acid medium of the LP (pH approx. 2.5). Through dissociation, a sufficient number of free ions are still present to continue influencing a decomposition of the HAN. Alternately, other complexes are only stable in organic systems and are, under certain circumstances, only suitable for the extraction of metal ions.

A further possibility lies in removing the metal ions through separation from the LP. Ion-selective, matrix-bonded substances here enter into consideration. A concomitant removal of the disturbing metal ions could be achieved via controlled precipitation reagents. If it is possible to demonstrate a reduction in decomposition, it would consequently be a worthwhile enterprise to pursue this line. This is why the attempt was made to influence the decomposition of copper- and iron-contaminated LP 1846 using complex-forming substances (Tab. 11). So precipitiation reagents, masking agents and complex-formers were selected to bond with the metal ions concerned.

The tests were carried out in ampoules at 90 °C (194 °F). 200 ppm complexing agents are used for 100 ppm metal ions. An exact quantity of 0.7 g LP was enclosed in these glass ampoules by welding their openings. In both of these measurement ranges, the results showed no stabilizing influence on the LP. These tests were then continued with other test substances, as well as at other concentrations.

5. Literatur

/1/ Klein, N.:
USA Ballistic Research Laboratory, personal communication, 1987

/2/ R.E. Lacey and S. Loeb:
Industrial processing with membranes, Wiley-Interscience, New York, 1972

/3/ EP 0147742, BASF, 8.7.1987, Stabilisierte Lösungen von Hydroxylamin und dessen Salzen in Wasser (Stabilized solutions of hydroxilamine and its salts in water)

/4/ US 35 44 270

/5/ Moews, P. C.
The Autoxidation of Hydroxylamine,
J. Inorg. Nucl. Chem., 1959, 11, 242

6. Annex (Tables and Figures)

Table 1: The influence of metals and alloys on the chemical stability of LP 1846. Accelerated storage test in ampoules at 90 °C (194 °F)

Table 2: The selection of suitable sealing materials

Table 3: The influence of sealing materials on the chemical stability of LP 1846. Accelerated storage test in glass ampoules at 90 °C (194 °F)

Table 4: The permeation coefficients of sintered PTFE (Hostaflon, manufactured by Hoechst AG) at room temperature in accordance with DIN 53380

Table 5: The temperature dependency of the permeation coefficients of PTFE (Hostaflon) with Helium

Table 6: The temperature dependency of the permeation coefficients P of amorphous PCTFE (Voltalef 300) for a number of gases.
Permeation coefficient x 10^{10}

Table 7: Gas fluxes Q (in cm^3/day) through PTFE and PCTFE sealing materials at $\Delta p = 5$ bar and at 25 and 90 °C (77 and 194 °F), calculated for flat sealing elements ($r_o = 6$ mm; $r_i = 4$ mm; $d = 2$ mm; $A = 0.63$ cm^2) of the testing apparatus

Table 8: The influence of 10 ppm metal ions on the storage life of LP 1846 (in ampoules) at 90 °C (194 °F)

Table 9: The influence of 100 ppm metal ions on the storage life of LP 1846 (in ampoules) at 90 °C (194 °F)

Table 10: Comparison of the relative decomposition times of LP 1846 in tests with ampoules

Table 11: The influence of stabilizers on the spontaneous decomposition of LP 1846 (in ampoules) containing copper and iron

Fig. 1: Expo nential temperature dependency of the permeation coefficients P of PCTFE (Voltalef 300) for N_2, O_2 and CO_2.
P in cm . mm /s . (cm Hg)

Fig. 2: DSC spectra of dehydrated NOS-365 as depending on the pH value. Weighed sample 15 mg; rate of heating 6° / min

Table 1: The influence of metals and alloys on the chemical stability of LP 1846. Accelerated storage test in ampoules at 90 °C (194 °F).

Metal/Alloy	Decomposition time in days	Relative decomposition time in %	Remarks
- (Original LP)	68,6	100	colourless
Gold	69,5	101,5	"
Silver	70,1	102,2	"
Mercury	68,2	99,0	"
Rhenium	1,5	2,2	"
Iridium	62,0	90,4	"
Platinum	56,7	82,7	"
Copper	1,6	2,3	green
Zinc	69,2	100,9	dissolved
Titanium	42,0	61,2	colourless
Tantalum	47,5	61,2	"
Chromium	23,4	34,1	"
Molybdenum	47,8	69,7	dissolved
Tungsten	34,4	49,7	colourless
Manganese	73,5	108,6	dissolved
Iron	1,0	1,5	yellowish green
Cobalt	55,6	81,0	pink
Nickel	56,8	82,8	green
Aluminium	73,0	106,0	colourless
Silicon	57,0	83,1	"
Tin	45,0	65,6	dissolved
Lead	74,0	107,4	colourless
Antimony	4,0	5,8	"
17/4 pH (1.4542)	15,7	22,9	colourless
V 2A (1.4541)	1,8	2,6	"
V 4A (1.4571)	50,4	73,5	"
30 CrNiMo8V (1.6580)	0,8	1,1	"
35 NiCrMoV125 (1.2760)	0,5	0,7	"

Table 2: The selection of suitable sealing materials

Chemical name	Abbreviation	Colour	Supplier
Ethylene-Propylene-Diene Copolymers	EPDM	black	Freudenberg, 6940 Weinheim, Postf.
Vinylidenefluoride-Hexafluorpropylene Copolymers (Viton)	FPM	black-brown	Ulman, 7032 Sindelfingen 6, Otto-Hahnstr. 17
Acrylnitrile-Butadiene Copolymers	NBR	black	Freudenberg (as above)
Silicone Resin	VMQ	red	Ulman (as above)
Ethylene-Propylene Copolymers	EP	black	Ulman (" ")
Polytetrafluoroethylene	PTFE (PT 950)	white	Gehrckens, 2080 Pinneberg, Postf.
Polytetrafluoroethylene	PTFE (TFM)	white	Beichler & Grünewald, 7121 Lochgau, Postfach
Tetrafluoroethylene-Perfluoroalkylvinyl Ether Copolymers	PFA, TFA	opalescent white	Beichler & Grünewald
Polytrifluorochloroethylene	PCTFE	transparent-turbid	Beichler & Grünewald

Table 3: The influence of sealing materials on the chemical stability of LP 1846.
Accelerated storage test in glass ampoules at 90 °C (194 °F)

Sealing material	Decomposition time in days		Relative decomposition time in %	
	in contact with LP	in gas space	in contact with LP	in gas space
- (original LP)	86,5	86,5	100	100
EPDM	6,2	20,7	7,2	23,9
FPM (Viton)	18,7	19,0	21,6	21,9
NBR	20,6	19,1	23,8	22,1
VMQ	44,8	61,9	51,7	71,6
EP	6,5	22,1	7,5	25,5
PTFE (PT 950)	86,2	not determined	99,6	not determined
PTFE (TFM)	88,6	"	102,4	"
PFA, TFA	90,6	"	104,7	"
PCTFE	94,0	"	108,6	"

Table 4: The permeation coefficients * of sintered PTFE (Hostaflon, manufactured by Hoechst AG) at room temperature in accordance with DIN 53380

Gas	Material: PTFE (Hostaflon)	
	TF 1740	TFM 1700
air	100	80
O_2	250	160
N_2	80	60
CO_2	700	450
He	2100	1700
Water vapor	0.03	0.03

Table 5: The temperature dependency of the permeation coefficients * of PTFE (Hostaflon) for Helium

Temperature °C	Hostaflon TF 1632
23	2400
35	3000
50	4100

* $P = Q \frac{d}{A \cdot \Delta p}$

Quantity	Q	A	d	Δp	P
Unit	$cm^3 \cdot day^{-1}$	m^2	mm	bar	$cm^3 \cdot mm \cdot day^{-1} \cdot m^{-2} \cdot bar^{-1}$

Table 6: The temperature dependency of the permeation coefficients * of amorphous PCTFE (Voltalef 300) for a number of gases. Permeation coefficient x 10^{10}

Temperature in °C	Gas					
	N_2	O_2	CO_2	H_2	H_2S	water vapor
0	-	0,07	0,35	3,20	-	-
25	0,05	0,40	1,40	9,80	-	1
50	0,30	1,40	2,40	24,0	0,35	10
75	0,91	5,70	15,0	-	2,0	28
100	-	-	-	-	-	100

$$^{*}\ P = Q \frac{d}{A \cdot \Delta p}$$

Quantity	Q	A	d	Δp	P
Unit	$cm^3 \cdot s^{-1}$	cm^2	mm	cm Hg	$cm \cdot mm \cdot s^{-1} \cdot (cm\ Hg)^{-1}$

Table 7: Gas fluxes Q (in cm^3/day) through PTFE and PCTFE sealing materials at $\Delta p = 5$ bar and at 25 and 90 °C (77 and 194 °F), calculated for flat sealing elements ($r_o = 6$ mm; $r_i = 4$ mm; $d = 2$ mm; $A = 0.63\ cm^2$) of the testing apparatus

Gas	PTFE (Hostaflon)				PCTFE	
	TF 1740		TFM 1700		Voltalef 300	
	25 °C	90 °C	25 °C	90 °C	25 °C	90 °C
N_2	$1.25\cdot10^{-2}$		$9.5\cdot10^{-3}$		$5.1\cdot10^{-5}$	$2.0\cdot10^{-3}$
O_2	$3.92\cdot10^{-2}$		$2.52\cdot10^{-2}$		$4.1\cdot10^{-4}$	$1.1\cdot10^{-2}$
CO_2	$1.1\cdot10^{-1}$		$7.1\cdot10-^{2}$		$1.4\cdot10^{-3}$	$2.7\cdot10^{-2}$
He	$3.83\cdot10^{-1}$	1.26				

Table 8: The influence of 10 ppm metal ions on the storage life of LP 1846 in ampoules at 90 °C (194 °F)

LP 1846 (Lot 49 - 1)		
Metal ions	Decomposition time in days	Relative decomposition time in %
Fe^{3+}	21,1	24,4
Ni^{2+}	65,3	75,4
Co^{2+}	61,1	70,6
Cu^{2+}	41,6	48,0
W^{6+}	89,0	102,8
Mo^{6+}	85,1	98,3
Mn^{2+}	87,0	100,5
Al^{3+}	68,9	79,6
Ce^{3+}	69,5	80,3
Pb^{2+}	75,1	86,7
Ag^{+}	80,5	93,1
Mg^{2+}	82,4	95,2
Cr^{3+}	79,6	91,9
Fe^{2+}	17,4	20,1
Ti^{4+}	59,6	68,8
V^{4+}	34,5	39,8
Zn^{2+}	72,7	84,0
Cd^{2+}	68,8	79,5
B^{3+}	82,7	95,5
Pd^{2+}	-	-
Zr^{4+}	86,4	99,9
Sn^{2+}	86,2	99,5
Bi^{3+}	80,8	93,3

Table 9: The influence of 100 ppm metal ions on the storage life of LP 1846 in ampoules at 90 °C (194 °F)

LP 1846 (Lot 49 - 1)		
Metal ions	Decomposition time in days	Relative decomposition time in %
Fe^{3+}	3,5	3,9
Ni^{2+}	80,7	88,9
Co^{2+}	73,0	80,4
Cu^{2+}	15,2	16,7
Hg^{2+}	64,1	70,6
W^{6+}	94,2	103,7
Mo^{6+}	62,6	68,9
Mn^{2+}	88,0	96,9
Al^{3+}	78,5	86,5
Ce^{3+}	82,6	91,0
Pb^{2+}	87,0	95,8
Ag^{+}	83,4	91,9
Mg^{2+}	87,3	96,1
Cr^{3+}	90,7	99,9
Fe^{2+}	3,5	3,9
Ti^{4+}	59,6	65,6
V^{4+}	11,9	13,1
Zn^{2+}	81,8	90,1
Cd^{2+}	78,1	86,0
B^{3+}	77,3	85,1
Pd^{2+}	31,4	34,6
Zr^{4+}	92,2	101,5
Sn^{2+}	83,6	92,1
Bi^{3+}	49,3	54,3

Table 10: Comparison of the relative decomposition times of LF 1846. Accelerated storage tests in glass ampoules at 90 °C. Metal ion concentrations in 2, 5, 10, 100 ppm.

Metal ions	Relative decomposition time in %			
	2	5	10	100
W^{6+}		120	103	104
Zr^{4+}			100	102
Cr^{3+}			92	100
Mn^{2+}			101	97
Mg^{2+}			95	96
Pb^{2+}		88	87	96
Sn^{2+}			100	92
Ag^{+}		99	93	92
Ce^{+}		98	80	91
Zn^{2+}		100	84	90
Ni^{2+}		97	75	89
Al^{3+}		88	80	87
Cd^{2+}		94	80	86
B^{3+}		97	96	85
Co^{2+}			71	80
Hg^{2+}				79
Mo^{6+}			98	69
Ti^{4+}			69	66
Bi^{3+}		100	93	54
Pd^{2+}				35
Cu^{2+}		59	48	17
V^{4+}		59	40	13
Tl^{3+}		36	24	4
Fe^{2+}		31	20	4

Table 11: **The influence of stabilizers on the spontaneous decomposition of LP 1846 containing copper ions and iron ions. Accelerated storage tests in glass ampoules at 90 °C.**

LP 1846 (Lot 49-1)		
Stabilizer content (200 ppm)	Decomposition time in days	
	Cu^{2+} (100 ppm)	Fe^{2+} (100 ppm)
- (without stabilizer)	15,9	3,5
Potassium fluoride	12,8	2,9
Tartaric acid	12,7	3,0
Citric acid	13,1	3,1
Phosphoric acid	12,2	3,5
8-Hydroxyquinoline	15,0	2,4
Nitrosophenylhydroxylamine (NH$_4$)	7,4	3,4
Dimethylglyoxime	12,6	2,7
Resorcin	12,1	2,1
Pyrocatechol	11,9	2,9
Morin	12,1	3,2
Alizarin	12,0	2,1
Alizarin monosulfonic acid (Na)	13,0	2,3
Ellagic acid	12,4	2,1
Dithizone	7,7	2,0
2,2'-Dihydroxydiphenyl	12,8	3,2
Aurintricarbonic acid (NH$_4$)	16,0	2,9
2-Hydroxy-5-methyl-1-azobenzene	11,7	2,9
5-Amino-salicylic acid	11,9	2,8
Ethylene diamine tetraacetic acid	6,4	3,2
3-Hydroxydiphenylamine	12,4	2,8
2,5-Dihydroxybenzaldehyde	13,1	3,2
Gallic acid	8,1	4,5
Dicyclohexyl-18-crown-6*	10,1	3,1
12-crown-4*	7,4	3,3
15-crown-5*	7,9	2,0
Dibenzo-18-crown-6*	7,2	2,1

* Supplier: E. Merck AG, FR Germany

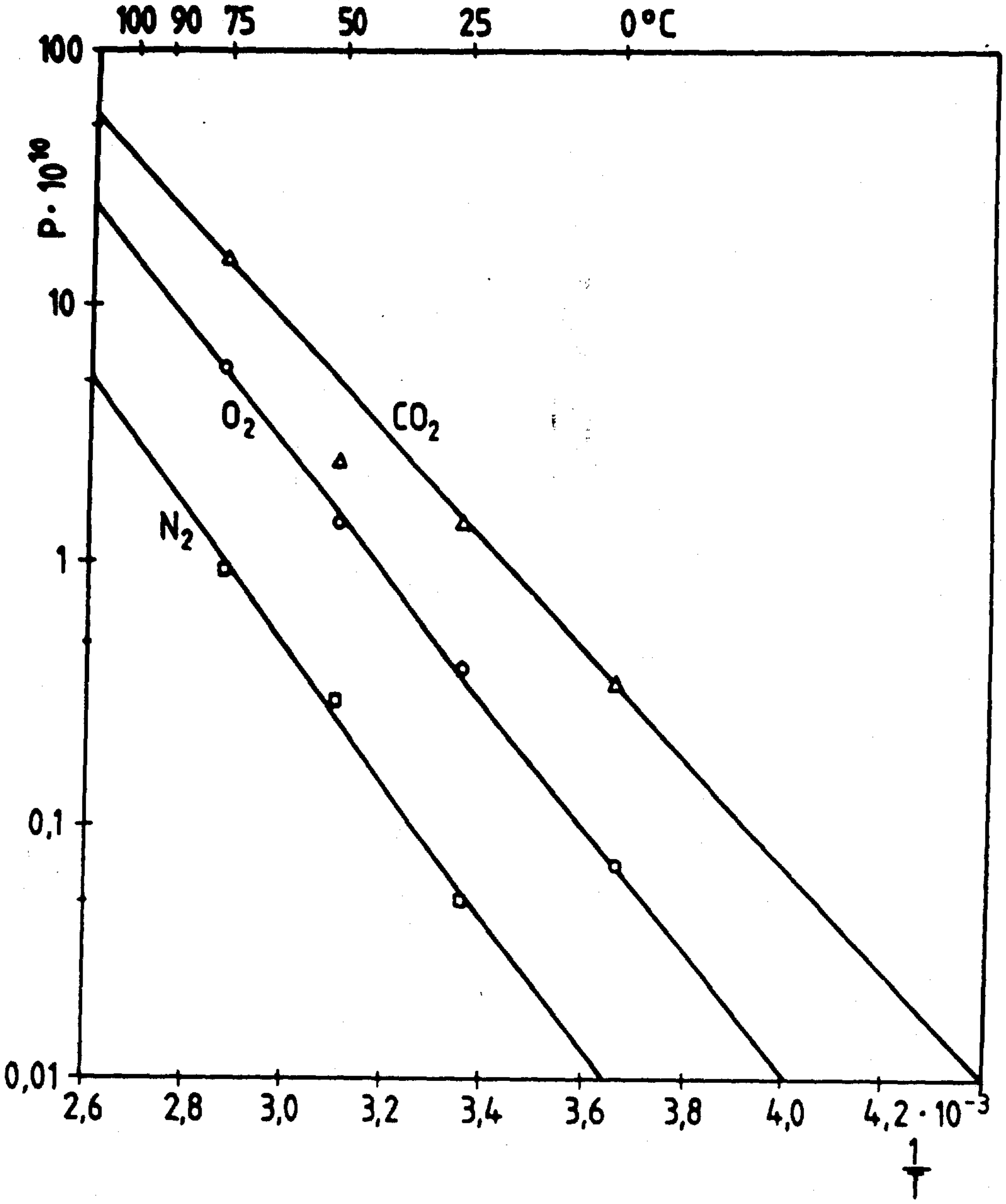

Fig. 1: Exponential temperature dependency of the permeation coefficients P of PCTFE (Voltalef 300) for N_2, O_2 and CO_2.
P in cm . mm /s . (cm Hg)

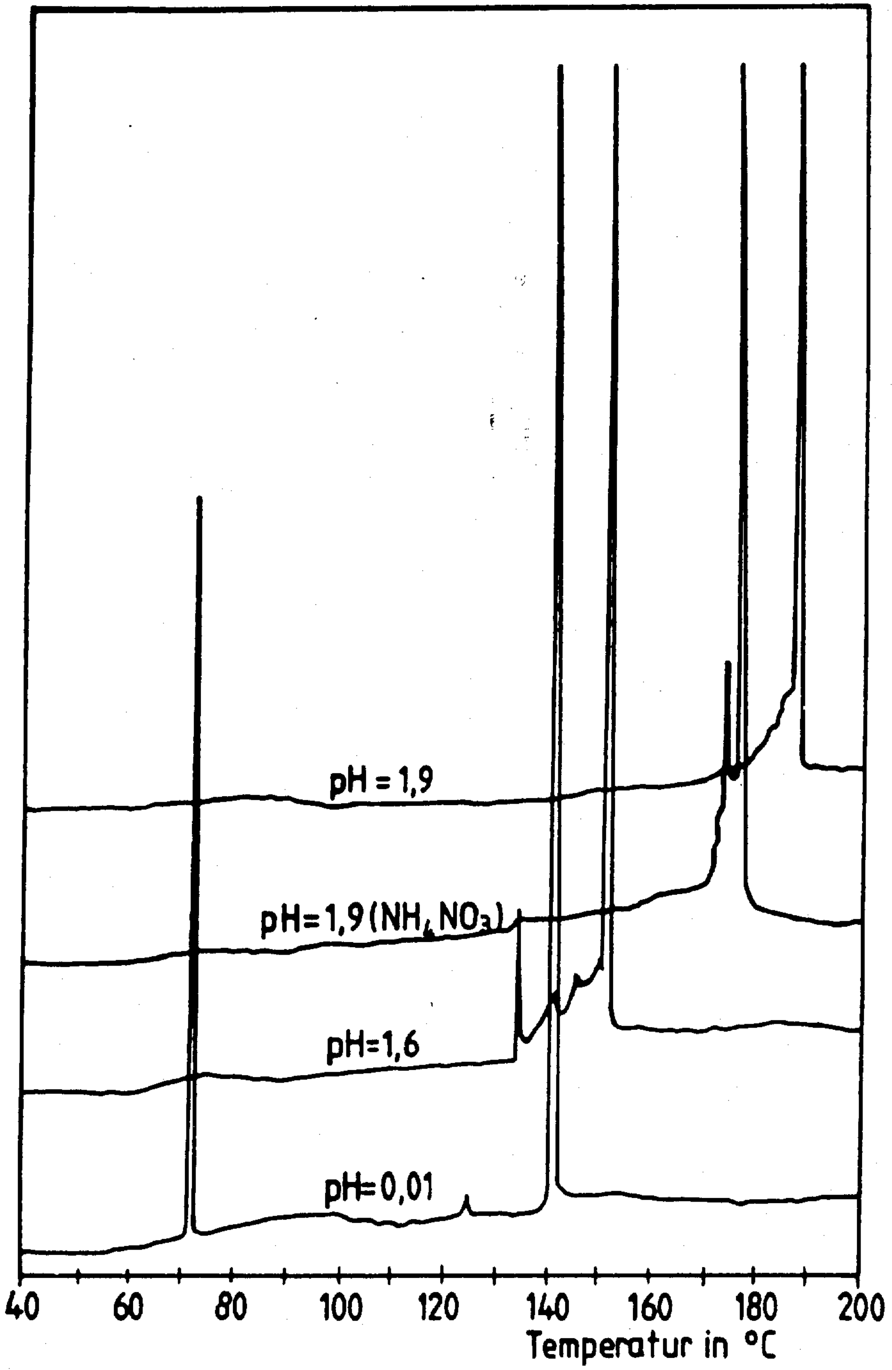

Fig. 2: DSC spectra of dehydrated NOS-365 as depending on the pH value. Weighed sample 15 mg; rate of heating 6° / min