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PROCESS FOR ASSESSING THE STABILITY
OF HAN-BASED LIQUID PROPELLANTS
Final Report

by

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

February 1989

United States Army

EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY

London England

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16 SUPPLEMENTARY NOTATION

17	COSATI CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Liquid Propellants (HAN-based); Decomposition mechanisms
			Long Term (Chemical) Stability; Stabilizers -
			Construction materials (metals,alloys(metal ions)plastomers)- cont'd on reverse

19 ABSTRACT (Continue on reverse if necessary and identify by block number)
Liquid propellants with hydroxylammonium nitrate (HAN) as a major component react to metallic
and non-metallic impurities by undergoing decomposition.

In this study, the effects of a number of metals (both as ions and as elements) and of a
number of plastics on the chemical stability as well as the long-term stability and/or
lifetime of the HAN-based monergol LP 1846 are examined.

For this purpose, two test methods were developed and applied: long-term storage at 90 °C
(194°F) a) in 5 cc sealed glass ampoules and b) in 3 cc glass containers equiped with miniature
pressure-transducers. The times up to the bursting of the glass ampoules or up to when a
specific pressure is reached constitute accurate parameters in assessing the stability of
the propellant.

The effects of the 25 types of metal ions we studied are given in 8 tables: iron, copper
and vanadium ions caused the greatest decomposition. In fact, vanadium ions were still
cont'd on reverse

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18 SUBJECT TERMS (continued)

Quantitative Chemical Analysis; Test Arrangements (Glass Ampoules, Glass Containers with Pressure Transducers)

19 ABSTRACT (continued)

effective at a concentration of 0.5 ppm. Other metal ions, such as those of magnesium, zinc and manganese, had no influence on the lifetime of the propellant.

We also examined 30 different metals and alloys in this context. Base metals entered into solution in the propellant, destroying its utility as a result. Two gunmetals and 3 stainless steels were subject to pronounced attack, thus greatly shortening the lifetime of the propellant.

On the other hand, gold, silver and tantalum remained without effect on the propellant and may consequently be used in constructing the necessary equipment.

Most flexible plastics for sealing elements were surprisingly unstable, causing marked decomposition and/or coloring of the propellant. Only polytetrafluoro-ethane (PTFE) and polytrifluorochloroethylene (PCTFE) were found to be inert.

The stability of the propellant also depends on its pH value: pH = 2.1 is the optimum value (measured after dilution with water).

To a certain extent, a number of aminophosphonic acids were found to act as stabilizers against metallic impurities. Dequest 2041 was particularly effective against iron and copper ions.

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component react with metallic and non-metallic impurities by under-
going decomposition.

In this study, the effects of a number of metals (both as ions
and as elements) and of a number of plastics on the chemical
stability as well as the long-term stability and/or lifetime of
the HAN-based monergol LP 1846 are examined.

For this purpose, two test methods were developed and applied:
long-term storage at 90 °C (194 °F) a) in 5 cc sealed glass
ampoules and b) in 3 cc glass containers equiped with miniature
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concentration of 0.5 ppm. Other metal ions, such as those of
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Base metals entered into solution in the propellant, destroying
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On the other hand, gold, silver and tantalum remained without
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(CONTENTS)

I.   Introduction

Liquid propellants with hydroxylammonium nitrate (HAN) as a major
component react very sensitively to specific impurities by under-
going decomposition reactions. We have found that this process is
particularly accelerated by iron, copper and vanadium ions. The
decomposition is a disadvantage for the storability, handling and
performance of the propellant. When kept in storage tanks, the
production of gas causes a pressure dangererously above the
atmospheric level.

The partial loss of a highly energetic component produces a
change in its ignition and burning behavior and a decrease in its
performance. Furthermore, decomposition reduces the pH value and
causes ammonium nitrate to be formed.

Impurities enter the propellant either from the raw materials due
to their handling. Up to now, the purest propellants have always
shown the greatest degree of stability. It has been possible, by
means of special processes such as the manufacture of HAN by
electrochemical methods as practiced by Messrs. OLIN /1/, to
fulfil the strict demands for purity in liquid propellants.

Our studies dealt with the effects of impurities on liquid
propellants and with the possibilities of stabilizing propellants
through the elimination or, alternatively, the complexing of the
impurities.

During the storage tests at increased temperature, the
composition of a propellant must not be changed due to any
exchange of materials with its surroundings (evaporation,
condensation, absorption). Such an exchange is prevented by using
sealed testing containers.

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As a criterium of stability, we chose the increase in gas
pressure in the container resulting from decomposition as
measured over time. Relative measurement values were obtained
through comparison with pure propellants or standard preparations
as reference.

Two methods were worked out to test storage life:

1. Storage of the samples at increased temperature in glass
    ampoules hermetically sealed by melting; the time up to
    bursting of the ampoules is measured;

2. Storage of the samples in sealed glass containers (with
    pressure sensor) at a raised temperatures we here measure the
    time required before a specified pressure (4 bar) is reached.

2.   Work schedule of Project DAJA 45-86-C-0056

The aim was to establish tests for HAN-based liquid propellants
to be named by the Ballistic Research Laboratory (BRL) in
Aberdeen Proving Ground, Md. (USA). The tests concerned the
chemical stability, the influence of impurities on storage
behavior, safety during handling, storage and attempts to improve
the chemical stability of the propellants.
For the quantitative determination of the individual components
of the propellants, analysis procedures had to be worked out.

In order to determine and assess the decomposition products and
the stability of the BRL monergol under consideration, the
following test procedures were to be carried out:

2.1 The development of analysis methods to determine the
     components, decomposition products and impurities in the
     monergol.

2.2 The determination of relevant test methods to simulate aging processes.

2.3 The provision of experimental proof of the influence of different impurities (transition metal ions) on the chemical stability, giving details on the maximum effective limit concentrations in each case through:

- The measurement of concentration changes in the individual components and determination of disintegration products (NH_4NO_3, HNO_3) during long-term storage in sealed containers at increased temperature;

- Measuring the pressure through time during long-term storage in sealed pressure containers at increased temperature.

2.4 The improvement of stability through optimization of the pH value, and proof of stability improvement via the determination of component decomposition during long-term storage at increased temperature.

2.5 The attempt to optimize the shelf life through the addition of different stabilizers (additives).

2.6 The measurement of gas composition after ignition in a burning chamber subjected to increasing burning chamber initial pressures will be the subject of a separate study carried out by Dr. Volk, D-7507 Pfinztal 1 (FRG) in 1989/90.

For the performance of the trials, original US samples of NOS-365 (Lot H 240) and LP 1846 (Lot 49-1) were made available to us. The analysis values we determined are given, in summarized form, in Table 1: here, by way of comparison, the analysis values for LP 1845 samples made by ourselves from HAN produced by the BASF

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(FRG) and Thiokol (USA). According to our analysis, the composi-
tion of the two US monergols, Lots H 240 and 49-1, differs from
the formulation given to a considerable extent.

3. Decomposition mechanisms of liquid propellant
    components

In their composition, the monergols based on HAN are balanced out
to a zero oxygen value.
According to N. KLEIN /2/, the reaction occurring when the
propellant is burned follows the equation:

  7 HAN + TEAN $\longrightarrow$ 6 CO$_2$ + 8 N$_2$ + 22 H$_2$O

This reaction is pressure-dependent. At a low loading density,
carbon monoxide and hydrogen are found in the fumen.

In the case of slow decomposition (aging), N_2O and NO are
produced in addition to the gases named above. As, during the
long-term storage of liquid propellants, HAN decomposes at a
considerably more rapid rate than TEAN, the equation cited is not
applicable for describing the actual decomposition processes.
Consequently, for recognition and assessment of the stabilization
possibilities, only a knowledge of those reaction mechanisms
which take place slowly (decomposition, aging) is able to help us
any further. A decomposition of an explosion type initiated by
ignition of the liquid propellants at high, rapidly increasing
pressures is therefore not able to provide us with valid
information on the development of aging processes.

The HAN component is - as already mentioned - the most sensitive
constituent in the monergols quoted. HAN decomposes very slowly
during storage. This process is accelerated by the presence of
heavy metal ions (Lit. /3/, /4/, /5/).

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The presence of the second component has no influence on the
start of decomposition. Therefore, it does not matter whether we
are dealing with a primary - as in the case of NOS-365 - or with
a tertiary ammonium salt - as in the case of LP 1846.

The decomposition of HAN is set off by a disproportionation
process as a result of which the instable intermediary compound
dihydroxylamine $NH(OH)_2$, plus ammonium nitrate and nitric acid
are formed from it:

$$2 \ NH_2OH \cdot HNO_3 \longrightarrow NH(OH)_2 + NH_4NO_3 + HNO_3 \qquad (1)$$

In the acid medium produced, the dihydroxylamine reacts through
renewed disproportionation with the formation of nitrogen dioxide
and water:

$$2 \ NH(OH)_2 \longrightarrow N_2O + 3 \ H_2O \qquad (2)$$

In a secondary reaction, the dihydroxylamine disproportionates to
HAN and nitrous acid:

$$2 \ NH(OH)_2 + HNO_3 \longrightarrow NH_2OH \cdot HNO_3 + HNO_2 + H_2O \qquad (3)$$

The nitrous acid is picked up by the HAN, ammonium nitrate or
oro   r ammonium salts: nitrogen dioxide is formed with the HAN
and   itrogen with the ammonium nitrate i.e.:

$$NH_2OH \cdot HNO_3 + HNO_2 \longrightarrow N_2O + 2 H_2O + HNO_3 \tag{4}$$

$$NH_4NO_3 + HNO_2 \longrightarrow N_2 + 2 H_2O + HNO_3 \tag{5}$$
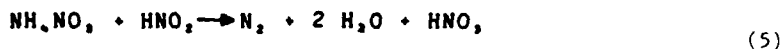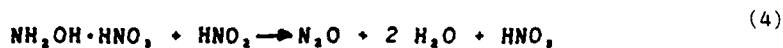
The formation of dihydroxylamine - and this is to be taken into careful consideration when handling the material - is encouraged by the presence of specific metal ions (Fe, Cu). These ions are easily capable of undergoing valency changes:

$$\tag{6}$$
$$NH_2OH \cdot HNO_3 + 2 Fe(NO_3)_3 + H_2O \longrightarrow$$
$$NH(OH)_2 + 3 HNO_3 + 2 Fe(NO_3)_2$$
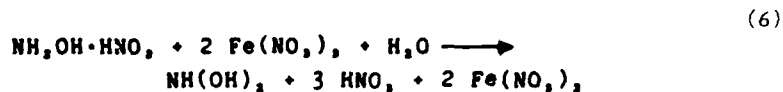
These metal ions are in turn oxidized by oxidizing agents such as HNO_3 or O_2,

$$3 Fe^{2+} + NO_3^- + 4 H^+ \longrightarrow 3 Fe^{3+} + NO + 2 H_2O \tag{7}$$

$$2 Fe(NO_3)_2 + NH_2OH \cdot HNO_3 + 2 HNO_3 \longrightarrow$$
$$NH_4NO_3 + 2 Fe(NO_3)_3 + H_2O \tag{8}$$
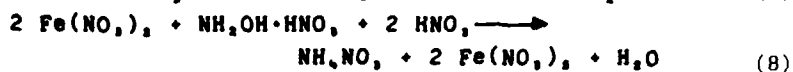
and the oxidation of HAN can once more take place in accordance with Equation (6).
Equations (7) and (8) basically describe the autocatalytic decomposition reactions observed in the monergols here involved.

The possibilities of finding stabilizers for liquid propellants containing HAN or of binding the metal ions, for example through the formation of complexes, are limited. In addition, a new reagent would have to be found for each of the unwanted elements.

The stability of metal complexes is furthermore reduced by the acid medium (pH $\cong$ 2.5). It is only possible to completely minimize autocatalytic decomposition by using particularly stable complex compounds or maintaining a very high degree of purity.

The primary amino group, such as that present in the IPAN of NOS-365, can be oxidized to a nitro group. Following aci-nitroalkane degradation (Nef reaction), acetone is formed. Dinitrogen monoxide is produced as a by-product.
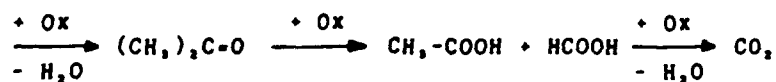
$$2\ \begin{array}{c}CH_3\\CH_3\end{array}\!\!\!CH-\overset{+}{N}\!\!\!\begin{array}{c}O^-\\\\O\end{array} \rightleftharpoons 2\ \begin{array}{c}CH_3\\CH_3\end{array}\!\!\!C=\overset{+}{N}\!\!\!\begin{array}{c}O^-\\\\OH\end{array}$$

$$\xrightarrow{H^+}\ 2\ \begin{array}{c}CH_3\\CH_3\end{array}\!\!\!C=O\ +\ N_2O\ +\ H_2O$$
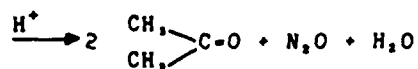
The primary amino group reacts with the nitrous acid in a known manner, whereby the primary amino group of the IPAN is diazotized; beside nitrogen, the occurrence of carbon dioxide, isopropanol, acetic acid and acetone is observed:

$$(CH_3)_2CH-NH_2\cdot HNO_3\ \xrightarrow[-\ HNO_3]{+\ N_2O_3}\ ((CH_3)_2CH-NH_2-NO)^+\ +\ NO_2^-$$

$$\xrightarrow{-\ HNO_2}\ (CH_3)_2CH-NH-NO\longrightarrow(CH_3)_2CH-N=N-OH \tag{9}$$

$$\xrightarrow[-\ H_2O]{+\ H^+}\ (CH_3)_2CH-\overset{+}{N}\equiv N\mathsf{I}\ \xrightarrow[-\ N_2,-\ H^+]{+\ H_2O}\ (CH_3)_2CH-OH\ +\ CH_2=CH(CH_3)$$

$$\xrightarrow[-\ H_2O]{+\ Ox}\ (CH_3)_2C=O\ \xrightarrow{+\ Ox}\ CH_3-COOH\ +\ HCOOH\ \xrightarrow[-\ H_2O]{+\ Ox}\ CO_2$$
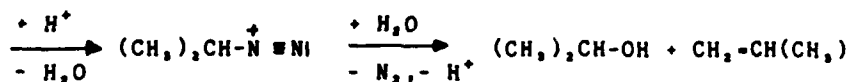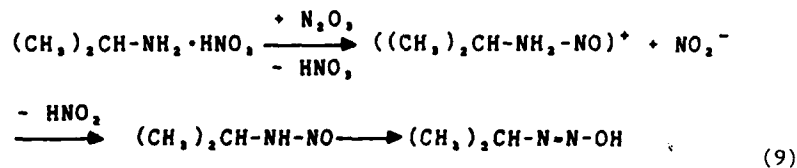
Parallel to this, ω-oxidation processes on the amine compound are also conceivable.

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No diazotizing reaction is possible in the case of the tertiary
ammonium nitrates present in the monergols LP 1776, LP 1845 and
others. In these compounds, however, there first of all takes
place a dealkylation through nitrous acid with the formation of
N-nitrous-amines (Lit. /6/, /7/) and the formation of aldehydes,
ketones or alcohols from the separated alkyl residue (Lit. /8/):

$$(HO-CH_2-CH_2)_3N + HO-N=O \longrightarrow$$
$$(HO-CH_2-CH_2)_2N-N=O + HO-CH_2-CH_2OH \tag{10}$$
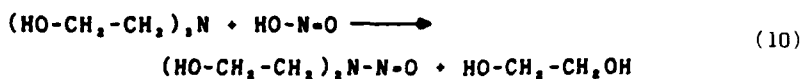
When metal ions (Cu^{2+}, Fe^{2+} etc.) are present, the nitrous amines
break down into secondary amine nitrate and nitrogen oxide (Lit.
/9/).

$$(HOCH_2-CH_2)_2N-N=O + 2HNO_3 + Fe^{2+} \longrightarrow$$
$$(HOCH_2-CH_2)_2NH \cdot HNO_3 + NO + Fe^{3+} + NO_2 \tag{11}$$

Over and beyond this, tertiary amines are subject to an oxidation
process at the alkyl residue (ω-oxidation) and a hydrolytic
splitting.

In this way, from less active tertiary amine compounds, the
corresponding primary and secondary amine derivates are produced,
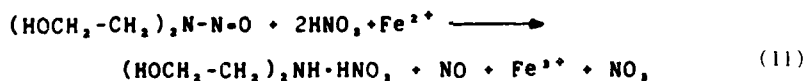together with a large number of consecutive products (Lit. /10/,
/11/, /12/) (see Fig. 2), which result in the final products NO,
N_2 and CO_2.

Although the HAN-containing monergols are made up of relatively
simple compounds, the presence of other consecutive products -
beside the large number of degradation products described - can
also be demonstrated. In the presence of HAN, the corresponding
oximes are formed from aldehydes and ketones. In accordance with
the Beckmann rearrangement, N-substituted carboxylic acid amides

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are produced from ketoximes: by acid catalytic hydrolysis, these
amides then split up into amines and carboxylic acid:

$$CH_3 - \underset{\underset{\textbf{INOH}}{\|}}{C} - CH_3 \xrightarrow{\textbf{H}^+} CH_3 - \underset{\underset{\textbf{H} - \overset{+}{\textbf{N}} - \textbf{OH}}{\|}}{C} - CH_3 \underset{\longleftarrow}{\longrightarrow}$$

Acetoxime   Iminium ion

$$CH_3 - \underset{\underset{\underset{\overset{|}{H}}{N - \overset{+}{O} - H}}{\|}}{C} - CH_3 \xrightarrow{-H_2O} CH_3 - \overset{-}{N} - \overset{+}{C} - CH_3$$
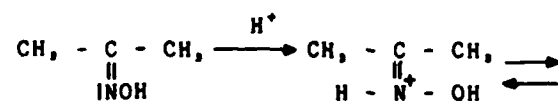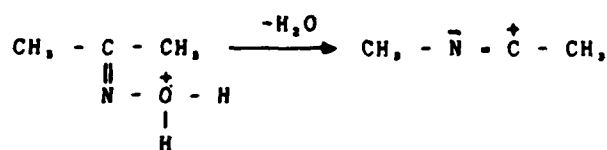
Oxonium ion   Carbenium ion

$$\xrightarrow[-H^+]{+ H_2O} \left[CH_3 - \underset{\underset{OH}{|}}{N} - C - CH_3 \right] \rightleftharpoons CH_3 - \underset{\underset{H}{|}}{N} - \underset{\underset{O}{\|}}{C} - CH_3$$
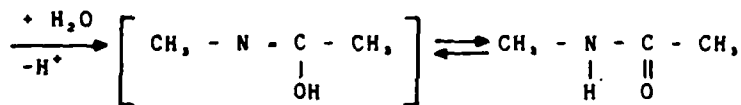
Enol-form   N-methyl-acetamide

$$\xrightarrow{+H_2O} CH_3-NH_2 + CH_3-COOH$$

In larger quantities, the formation of the consecutive products
described in the liquid propellant is only observed under extreme
conditions. Under combustion, however, they are capable, as
intermediary products, of influencing the burning behavior.

4. Test arrangement to determine the chemical stability of
    liquid propellants at raised temperatures

In the case of solid propellants, testing of the chemical
stability is laid down by work specifications. Parameters for
stability assessment can be obtained, for example, from tests on

weight loss, stabilizier decomposition, demonstrating the
presence of decomposition products, rise in pressure or also from
the heat developed during thermic loading.

In the case of liquid propellants, however, it has not been
possible to lay down any specific test specifications up till
now. Test procedures - analogous to those for solid ones - are
problematic for liquid propellants: this is because, during long-
term storage, a continuous evaporation of the readily volatile
components takes place, producing - instead of the originally
insensitive propellant - an instable material sensitive to
manipulation. For this reason, a test procedure must be applied
which prevents a partial evaporation of substances from the
liquid during the simulation of aging processes. From this it
follows that the test substances must be enclosed in a hermeti-
cally sealed system capable of withstanding the pressure
occurring during the storage period. All test methods in which
this problem cannot be mastered are only capable of producing
inaccurate results.

In order to assess their storability, the propellant samples are
subjected to a simulated aging process at a raised temperature.
Storage of the propellant samples at increased temperature takes
place in a pressure container in order to prevent the evaporation
of water from the propellant mixture.
It is the aim of our work to propose processes for testing chemi-
cal stability in which long-term storage of liquid propellants in
a closed system can be carried out under conditions not present-
ing any risk.

4.1   Storage in glass ampoules

In order to assess the influence exerted by different variables
on the stability of a propellant, such as the type and concentra-
tion of metal ions, pH value and stabilizers, were subjected

samples to an artificial aging process in hermetically sealed pressure containers to prevent water from evaporating out of the test liquid.

We found that glass ampoules holding a volume of 5 cc and having walls 0.6 mm thick were suitable as containers. The best ampoules were those commercially available and manufactured on an industrial scale.

The filled ampoules were closed by melting. Due to the formation of decomposition gases, the pressure in the ampoules rose gradually until they burst at approximately 10 bar. The time measured up to bursting point was taken as a relative stability value. At a first glance, the process just described may seem a somewhat approximate method: however, when a number of test conditions are strictly observed, such as conformity of initial weighed samples (0.7 g), the use of all (high-quality medical) ampoules from the same batch and the observation of extreme cleanliness during preparation of the samples, parallel tests showed a satisfactory agreement: at no point did deviations exceed 20 %. The validity of the values obtained was high. For example, the bursting time of the ampoules was shortenend from 86 to 21 days when LP 1846 with impurities of 10 ppm iron ions was used in place of the pure substance.

Each individual measurement value was obtained as an average parameter over 5 parallel tests. Although it would have been more desirable for statistical reasons, we nevertheless had to abandon employing a larger number of parallel reference samples due to economic considerations. Only when a number of "exceptional cases" occurred did we have to repeat the measurement series.

A premature bursting of the ampoules was a result of improper closing by melting. Deviations in wall thickness of the ampoules, which are unavoidable due to industrial production methods, had no noticeable influence on the results. Apart from this, the

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pressure increase rate accelerated rapidly during the final stage of the test storage period.

It was possible to store up to 25 samples simultaneously at 90 °C (194 °F) in block thermostat arrangements. Assessment of the bursting times took place at intervals of 24 hours. The period of time up to decomposition of the samples stored under isochoric and isothermic conditions is a measure for the chemical stability of liquid propellants.

A further simple possibility for testing monergols in glass ampoules consists of storing them in heating block thermostats for predetermined periods of time (e.g. 5, 10 and 15 days), whereby the tests are discontinued prior to destruction of the containers and the samples subjected to thermic loading in this way analyzed afterwards.

The ampoules are cooled in liquid nitrogen, opened and their components analyzed. By this method, the degree of decomposition can be determined as dependent on storage duration.

The use of glass ampoules for testing the effect of materials, impurities and stabilizers was found to be very advantageous for highly comprehensive test programs and for initial test series. As compared with the second test method described below in Section 4.2, the following advantages were found:

    I. No problems with sealing elements, sealing materials and metallic materials;
   II. No complicated measuring equipment is required;
 III. They are simple to handle;
  IV. The apparatus required is economical (relatively cheap);
   V. Measurement accuracy is increased due to the possibility of a large number of parallel trials.

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By contrary, the following disadvantages could not be overlooked:

I.   The pressure development cannot be controlled;
II. There is no possibility of preparing pressure/time diagrams
     and thus no chance of comparison with values from chemical
     analysis;
III. Glass fragments and propellant residues are propagated upon
     bursting of the ampoules, in addition to which nitrous gases
     are released.

4.2   Storage in glass containers with pressure sensors

During the aging of liquid propellants at increased temperature,
gases are constantly formed. In a closed system, these decomposi-
tion products cause a constant increase in pressure which can be
measured continuously with an appropriate pressure sensor. This
method has the advantage that changes in the test substance can
be observed and recorded directly as a factor depending on time.

The tests are discontinued and the sample residues subjected to
analysis when a predetermined pressure is exceeded.
The time up to the point when a specific pressure is reached
(4 bar, compare below) is taken as a relative parameter for the
stability of a liquid propellant.

Fig. 3 gives detailed information on the measuring equipment. The
glass containers with an exterior diameter of 12 mm, a length of
50 mm and a wall thickness of 1.5 mm had a volume of 2.9 cc and
were capable of withstanding an interior pressure of at least 30
bar. The glass containers were equipped with screwcaps (German
standard GL 14 thread in accordance with DIN 168). The pressure
sensors were fitted in a hole drilled through the sealing cap.

The pressure sensors were Sensotec subminiature pressure transdu-
cers model 81 G (manufactured by Sensotec Inc. and supplied by

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Messrs. H. Burster, FRG) with a foil-type strain gauge full
bridge and capable of measuring pressures up to a maximum of 5
bar. The transducer casing is made of stainless steel of the type
17-4 PH (German standard, Mat. No. 1.4542), compare Table 2. To
protect against corrosion, the casings had previously received a
thick plating of gold (compare Section 4.2.1.1) and been sub-
jected to final calibration. For this, an automatic pressure
calibration apparatus type EPK 20, as manufactured by Messrs.
Promotek, was used.

The pressure was recorded via a UPM 60 multisite measurement unit
manufactured by Messrs. Hottinger Baldwin Meßtechnik (FRG). This
universally applicable unit is designed to accommodate a maximum
of 60 measurement leads and is equipped with integrated measuring
amplifiers, AD transducers and a microprocessor measurement
value processing system, V 24 computer interface and paper strip
printer.

The weight of the samples was assessed at exactly 1 gram. For
safety reasons, we do not recommend larger weights of sample. The
glass containers with the samples and the attached pressure
transducers were maintained isothermically during storage in a
thermostatically controlled heating block. This is to prevent
partial separation of the propellant constituents due to
evaporation of water and condensation at cooler parts of the
containers.
For reasons of safety, a pressure of 4 bar was fixed as the
maximum pressure limit.

The measurement values recorded are shown as pressure/time
diagrams, thus clearly showing the progression of decomposition
through time.

For a continuous pressure measurement during the aging of liquid
propellants in pressure containers, the following advantages are
found:

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   I. Pressure/time diagrams can be obtained;
  II. Both the control of pressure and recognition of critical
      pressure values in good time are possible;
 III. The possibility of comparing the composition (analysis) of
      the sample residue and the quantity of decomposition gases;
  IV. At a pre-specified pressure, gas analyses can be carried
      out, for example with a mass spectrometer.

However, this measurement method has the following disadvantages:

   I. A failure of the sealing elements may result in a
      spontaneous decomposition of the propellant, thus destroying
      the sensors;
  II. Sophisticated measurement electronic equipment is necessary;
 III. The expensiveness of measuring apparatus and pressure
      sensors set a limit to trials in series.

4.2.1   Selection of metallic and non-metallic materials for
         the construction of the test apparatus

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 test
apparatus exert no influence on the life term of propellant
samples.

Preliminary trials with various pressure sensors (Sensotec, Inc.)
had shown that - after the influence of NOS-365 at 90 °C (194 °F)
over a period of several months - the surfaces of the sensors
showed corrosion phenomena. Apart from water vapors, hydroxyl-
amine and nitric acid also occur in the containers in the gaseous
phase during the storage of monergols containing HAN at raised
temperature. The presence of these substances was found in the
distillate of LP 1846 via potentiometric titration. Consequently,

we first tested the interactions between metals, alloys and sealing materials on LP 1846.

The test procedure described in Section 4.1 with the enclosure of the samples in glass ampoules shows its particular value in that only the high-quality medical glass is in actual contact with the propellant samples. As described in Section 3 and was also found by testing, glass does not limit the stability of HAN-based propellants.

We therefore made use of the glass ampoule tests as an arbitration method on the metallic and non-metallic materials used for the construction of the test apparatus with glass containers and pressure sensors, which is described in Section 4.2. As the results of these stability tests are also important for a later use of the propellant in question (this also including e.g. storage, transport and use in liquid gun propellant (LGP)), other metals and metal alloys not usually used in the test apparatus were also examined in this way.
To retain consistency, the results of these tests are not given until later, in Section 6, whereas we shall here only consider those aspects directly related to the apparatus design and/or construction.

4.2.1.1 Metals and alloys

It can be seen from Table 3 that the stainless steel of the type 17-4 PH (German Standard No. 1.4542), from which the casing of the Sensotec pressure sensor is made, reacts with propellant LP 1846. The life term of the propellant sample is thus shortened by 23 % of its original value.

We made no attempts to passivate stainless steels against LP 1846 at the ICT. Practical experience in this field was, however, made at the BRL /13/.

Long-term storage tests on LP 1846 when in contact with metallic
materials (Table 3) have shown that gold causes no reduction at
all in the storage life of the propellant. Consequently, the
pressure transducers, made of construction material 17-4 PH were
galvanically gold-plated. Preliminary coating was with Au/Co
alloy, 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 tightness. 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 transducers and
their connecting cables during the galvanization process and
subsequently removed.

4.2.1.2 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:

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

II. 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 10
different plastomers and elastomers, listed and described in
Table 4, were tested in glass ampoules.

The tests showed that only Teflon (PTFE - PT 950; PTFE-TFM),
Teflon-PFA and polytrifluorochloroethylene (PCTFE) are here
applicable. With these materials, the life time of the samples
reached that of the original LPs.

4.2.1.3 The permeation of gases through high-polymer
          substances

Apart from their chemical stability as well as their compatibili-
ty with the liquid propellant, selection criteria for materials
used in sealing glass pressure containers also include their per-
meability to gases and their viscous flow behavior.
All plastics are more or less permeable to gases. Taking a layer
made of plastic with a thickness d and surface A (example: planar
membrane), a pressure difference Δp between the two sides of a
membrane causes a gas flow Q from one side to the other. This trans-
port process is called "permeation". If Δp is not too high, the
permeation process may be described by the linear relation /14/:

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

Here, 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 Kelvin, and P_0 a constant. When ln P is plotted
versus 1/T, the equation produces a straight line. For the calcu-
lation 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 calcu-
lations 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, in-
coherent units are often also used in practice, so that a conver-
sion 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 compari-
son in Tables 6 and 7. The manufacturer gives the permeation co-
efficient 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 8. Fig 5 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:

$$A = \quad = 2\pi\ r_m h = 0.63\ cm^2;$$

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

For sealing elements made of PTFE and PCTFE with these dimensions
the permeating gas fluxes were calculated in cm^3/day for tempera-
tures of 25 and 90 °C (77 and 194 °F): these values are given in
Table 9. Calculation is based on the permeability coefficients
converted according to Fig. 5 as given in Tables 6 and 8.

It can be seen from Table 9 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, FRG) are, however, slight (Fig. 5; Tab. 9)

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 4 bar. In the original samples of LP 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 4 bar toward the end of

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*) I.e, the arithmetic mean values of N_2, O_2 and CO_2.

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.

4.2.1.4 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 manufactu-
rers 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 4.2.1.3 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, the chemical stability of
liquid propellants and the influence of stabilizers on the
storage life of liquid propellants was determined.

Difficulties were encountered at times with the sealing of the
test apparatus. A part of the apparatus leaked during long-term
storage: pressure did not continue to rise. The cause for this
can be found in the flow behavior of the sealing materials used.
Plastomers are subject to deformation under stress. The extent of
stress-induced deformation (7 MPa over 24 hrs at 25 °C / 77 °F)
is 2.5 % for PTFE TF 1740, 1.5 % for PTFE TFM 1700, and 1 % for
PCTFE Voltalef 300. In the test apparatus (Fig. 3), PCTFE sealing
elements, i.e. plastomer materials with a very low deformation
under stress were used.

To increase the tightness, i.e. the sealing efficiency of the testing apparatus, a number of variants were worked out for this purpose:

- The pressing of the flat sealing elements by spring-loaded elements,

    and

- The exchanging of plastomers for elastomers.

Spring-loaded sealing elements

As alternative to a screw fitting of the glass container with melamine resin screwcap (Fig. 3), we constructed a sealing device consisting of a tightening frame and a screw-mounted spring. The screw was operated by a milled head. However, the spring was found to be too weak, and we encountered problems in the housing of the spiral spring. We considered exchanging the coil spring for a bank of cup springs. Cup springs are suitable where a greater spring force is required over small lengths. In view of the high expenditure of production for the tightening device (60 separate units were needed), we looked for more simple solutions. The closest alternative seemed to be the replacement of the steel springs (coil or cup springs) by rubber washers.

Using the test apparatus according to Fig. 3, it could be possible to incorporate rubber washers (thickness approx. 1 mm) between the screw cap and the pressure transducer. However, the maintenance (i.e. no worsening) of the elastic properties (tension and compression behavior) during long-term storage at increased temperatures is the prerequirement for this provision.

Elastomers as sealing materials

As sealing materials for the testing apparatus here under
consideration, elastomers only come into the question if they
exert no influence whatever on the chemical stability of the
liquid propellants, i.e. if they are compatible with the
propellant and furthermore possess a low gas permeability.

Simultaneously with the development and testing of sealing
elements, therefore, we also tested the compatibility of
peroxidic cross-linked Viton (Viton GF) and of perfluorated
hydrocarbon (Kalrez 4079) with the liquid propellant LP 1846.
For this purpose, the sealing materials were enclosed in the glass
ampoules tog'ther with the LP 1846 and stored in heating block
thermostats at 90 °C (194 °F). The time up to bursting is a
measure for the compatibility of the material with the propel-
lant. This is related to that of pure propellant. The storage
trials showed that the life term of the liquid propellant is
considerably shortened by contact with the elastomers.
In the case of Kalrez, this dropped to 48 % and in the case of
Viton even to 25 % of pure propellant (Table 5). Apart from
determining compatibility with LP 1846, the permeation of gases
was also calculated for the elastomers Viton GF and Kalrez 4079.
The permeation - calculated from the example of 12 x 8 x 2 mm
ready-made sealing elements for nitrogen at 25 °C (77 °F) - is
greater by a factor of 80 times in Viton and by a factor of 600
times in Kalrez than in PCTFE.

Both elastomers, therefore, do not come into consideration as
sealing materials for long-term testing apparatus units, first of
all on account of their bad compatibility with the propellant,
i.e. due to a shortening of the life term of LP 1846, and on the
other hand because they have a high gas permeability.

After previous selection of a suitable sealing from the informa-
tion supplied by manufacturers and through calculation, a special

trial was carried out to test the tightness of glass containers
with pressure sensors, whereby a determined quantity of gaseous
nitrogen was produced through the reaction of a titrated sodium
nitrite solution with solid amidosulfonic acid (in excess) in a
glass container equipped according to Fig. 3.

The amidosulfonic acid was located in a small glass crucible
which could be magnetically moved and arrested (micromagnetic
stirrer in glass container, Alnico magnet on the outside). Thanks
to this technique we were able to produce the gas once the top of
the container had been screwed on tightly.

The signal from the pressure sensor was indicated via strain
gauge signal conditioner and amplifier. The glass container was
kept at room temperature.
Table 10 shows the pressure in the glass container measured over
a period of 36 days. The maximum difference between the pressures
measured was approx. 6 - 7 %; a systematic, time-dependent drop
in pressure could not, however, be recognized.

The pressure was corrected according to the equation of state for
ideal gases. Other corrections, such as the solubility of the
nitrogen in the aqueous solution and the partial pressure of the
water vapor were not taken into account.

Following these measurements, the thickness of the PCTFE sealing
elements had been reduced from 2 to 1 mm (12 x 8 x 1 mm).
A tension wrench was used to tighten the plastic screw caps. As a
result of these improvements, the use of spring-loaded sealing
units and of elastomers as sealing material was no longer
necessary.

4.3   Storage in glass ampoules with strain-gauges

According to the test arrangement described in Section 4.2 above,

the pressure sensor and the sealing are located directly over the
test solution and are subjected to the temperature and the acid
atmosphere of the monergol during the entire storage period. It
is here a prerequirement that the materials of the pressure
sensor and the sealing material be insensitive to humidity and
gases produced by decomposition to avoid the release of ions
which would in turn accelerate decomposition of the propellant
tested. In order to exclude these disturbing factors during the
test process, materials are used for the pressure sensors and the
sealing which are compatible with the liquid propellant to be
tested and exert no influence on the life term of the propellant.

As an alternative to measurement of the pressure rise with the
sensor fitted in the test container, the pressure can also be
measured with the aid of strain gauges adhered to the outside
wall of a thin-walled glass ampoule (< 0.5 mm). The advantage of
this test procedure is found in the fact that the strain-gauge
pressure sensor does not come into contact with the liquid test-
ed, thus excluding the possibility of results being influenced by
metal ions from the sensors used.

On account of the interior pressure generated by the decomposi-
tion gases, the wall of the molten-sealed glass ampoule is sub-
jected to a transverse and longitudinal expansion.

Test measurements in half-bridge circuits with temperature
compensation were carried out in which an active strip was
adhered to the molten-sealed glass container and a compensation
strip onto an empty, open test container. This method can be
employed for evaluation with the UPM 60 multi-site measurement
unit internally for 10 measurement points in each case. Further
sample tests in half-bridge circuitry without temperature
compensation were carried out in which a fixed resistance was
used in place of the compensation strain gauge. The measurements
showed that - in both test arrangements - the strain gauge
sensitive to longitudinal force showed a low rate of expansion

but that sensitive to transverse forces recorded relatively high
expansion values of 12.5 μm/bar. Fig. 4 shows the pressure
curves. These testing methods provide us with statements on the
decomposition and influences on the stability of monopropellants
containing HAN. They show changes during the reaction period with
high sensitivity. Disturbances from metal ions released from the
material of the pressure sensor used and the exertion of an in-
fluence of the sealing material on the life term of the propel-
lant are here excluded.

As a disadvantage in the storage of monopropellants in glass
ampoules with strain gauges attached to them by adhesion, we
found that each glass ampoule had to be calibrated separately for
the test temperature coming into consideration each time.

We therefore preferred monitoring the rise in pressure during
long-term storage with pressure sensors (Section 4.2).

5.   Quantitative propellant analyses

5.1   Propellant components

Examples for the composition of liquid propellants are given in
in Fig. 6. All propellants contain hydroxylammonium nitrate. The
nitrate of an organic amine is the second propellant component.
The first amine selected was isopropylammonium nitrate (IPAN). It
was then found that IPAN has bad burning kinetics /13/. Its place
has been taken by triethanolammonium nitrate (TEAN). HAN and
amine nitrate are liquified by adding water. In view of its
relatively low water content of approx. 20 % by wt., the liquid
propellant mixture should rather be called a melt than a
solution.

Ammonium nitrate (AN) is not listed in Fig. 6. It either occurs
as an impurity in the components or it is produced as a decompo-

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sition product. Even slight quantities of AN are supposed to
raise the freezing point of the propellant /13/.

5.2   Methods of determination

Separation and quantitative determination of the propellant com-
ponents by gas chromatography appears to be possible. For this
purpose, the amines should be liberated in a preparatory column
filled with alkalines. However, it is questionable whether the
hydroxylamine would survive the separation process without decom-
position. No examples are given in literature, and we did not
carry out experiments of our own.

Ion chromatography is without doubt a conserving separation pro-
cess, which has been worked out for analyses in the ppm range.
The necessary sample volume is approx. 100 microliters ($=$ 0.1
ml). The individual ions are detected quantitatively by conducti-
vity measurements. Here the accuracy of analytical determina-
tions, however, is not reached.

For the determinations in this study we chose the method of
volumetric analysis. These are accurate (generally better than 1
%). There are often several determination processes for one
component (e.g. analysis via neutralization, oxidation and
precipitation), which considerably improves reliability.

Reference solutions, which are difficult to prepare or also have
to be controlled by volumetric analysis, are not necessary. For
the propellants, a number of compounds (generally three) have to
be titrated one after the other. This is why simple apparatus and
indication processes (chemical indication) are not sufficient.
Potentiometric determination of the equivalence point is the most
suitable method /15/.

Time is saved by using automatically recording titration

equipment. Evaluation of titration curves by calculation is
difficult where the points of inflection are weak. Therefore,
the use of microprocessor-assisted titration and potentiometric
equipment is not only recommendable but necessary /16/.

5.3   Acid/base titration and pK values

All propellant components given in Fig. 6 and in Section 5.1 are
salts formed from a relatively strong acid (in this case nitric)
and relatively weak bases (in this case organic and inorganic
nitrogen compounds).

In aqueous solution, these salts yield an acid reaction: the pH
value is below 7. The salts can therefore be titrated with a
strong base, e.g. potassium hydroxide solution. The bases are
then liberated from the salts (substitution titration). In the
relatively stronger bases such as ammoniac and primary organic
amines, the equivalence point is far into the alkaline range
(above pH = 10). The end point can then no longer be determined
with color indicators such as e.g. phenolphthalein.

The acidity of ammonium- and hydroxylammonium salts can be
increased through derivative formation. The end points are then
shifted towards lower pH values, so that simultaneous determina-
tions are either facilitated or made possible.
Ammonium salts react with formaldehyde to form the very
weak base hexamethylene tetramine:

$$4 \ NH_4NO_3 \ + \ 6 \ CH_2O \longrightarrow N_4(CH_2)_6 \ + \ 6 \ H_2O \ + \ 4 \ HNO_3. \quad (12)$$
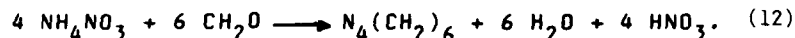
The sample can be titrated after the addition of formaldehyde
with potassium hydroxide and phenolphthalein as indicators /17/.

The reaction is specific for ammonium salts and ammoniac. Organic
amines do not react under these conditions with formaldehyde.

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Hydroxylammonium salts react with aldehydes and ketones to aldoxims or ketoxims respectively. For example, formaldoxim or acetoxim is obtained from hydroxylammonium nitrate with formaldehyde or acetone:

$$H_2NOH \cdot HNO_3 + CH_2O \longrightarrow H_2C=NOH + H_2O + HNO_3, \qquad (13)$$

$$H_2NOH \cdot HNO_3 + (CH_3)_2CO \longrightarrow (CH_2)C=NOH + H_2O + HNO_3. \qquad (14)$$
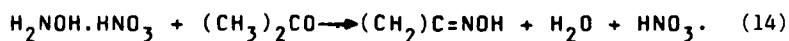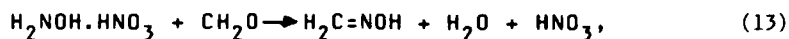
The individual types of ions can be determined in mixtures from different acids or bases one after the other via titration if the final potentials are sufficiently different from each other. These potentials depend on the dissociation constants K_A and K_B of the relevant acids or bases.

For reference purposes, the dissociation constant or pK value analogous to the pH value is used. This is defined as

$$pK_A = -\log K_A \text{ or } pK_B = -\log K_B.$$

The equation:

$$pH = pK_A - \log(C_{acid}/C_{salt}) \qquad (15)$$

exists between the pK value of a weak acid or base in aqueous solution and the measurable pH value of the solution. C_{acid} and C_{salt} are total concentrations of an acid and its salt known from initial weight or analysis. Activity coefficients are negligible due to the low concentrations involved. Where the concentrations of acid and salt are equal, the log in Equation (15) assumes the value zero. In such a case pH = pK_A or pH = pK_B. The values of pK can then be measured via potentiometric titration: the pK value is equal to the pH value measured at half neutralization.

The following relation exists between pK_A and pK_B values:

$$pK_W = pK_A + pK_B. \tag{16}$$

pK_W is the negative log of the ion product of water:

$0.68 \cdot 10^{-14}$ $mol^2 \cdot dm^{-6}$; $pK_W = 14.17$;

values apply for 20 °C (68 °F).

In Table 11, the values for K_A, pK_A and pK_B (columns 2, 3 and 4) have been put together for the most important propellant components.

The values are determined through neutralization titration using the "Titroprozessor 636", whereby the nitrates of the amines (column 1) were titrated with potassium hydroxide. First the pK_A values (column 3) are obtained as the pH values measured once half the final point volume of standard solution had been used up /20/.

The combined glass electrode used for measuring was calibrated through comparison with two buffer solutions of a known pH value /20/.
For the pK_A determinations, as far as possible, the same test conditions were adhered to as in later measurement analyses (quantity, volume and temperature of the sample; normality of the standard solution).

The pK_B and K_A values are calculated from the pK_A values. For reference, the pK_B values obtained from literature were entered in Table 11 (column 5). Further details on the measuring procedures used to obtain these values (potentiometry, conductivity measurements) are not known. In the case of hexamethylene tetramine (3rd row), the two literature values differ quite considerably. Under these conditions, the agreement between columns 4 and 5 is to be regarded as satisfactory.

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The acidity of the amine nitrates can be seen from <u>Table 1</u>: the propellant components are arranged according to decreasing acidity, i.e. with a decrease in the dissociation constant K_A.

Simultaneous determinations of a number of acids or bases are only possible if the dissociation constants are greatly different. This difference should be by 4 /17/ or at least 3 /13/ times the power of ten. The situation is even less favorable where a type of ion is only present in low quantities in a mixture such as e.g. NH_4^+ as an impurity in HAN. The equivalence point is then covered by interference of the titration curves. Nevertheless, with microprocessor-assisted titration apparatus it is still possible to identify weak and closely adjacent final titration points /16/.

5.4   The Titroprozessor 636

The Titroprozessor 636, Program Group P 100, is an analog/digital measurement and titration unit for universal potentiometric application.

The unit is equiped with a 16-bit microprocessor enabling special performance in processing and evaluating signals, data output and the control of peripheral equipment.

Titration can be carried out in three different operation modes:

- Dynamic titration with variable volume steps: few measurement points with stretched and many measurement points with greatly curved sections;

- Dynamic titration with variable volume steps up to the preselected final point; the addition of reagent is interrupted when a preselected final point or potential is reached;

- Monotone titration at constant volume steps: measurement point
  accumulation with low curvature.

The evaluation programs to calculate the point of equivalence
from the titration curves are based on methods known from
literature /15/. Where necessary the manufacturer (Metrohm) has
applied modified evaluation methods /20/.

The manufacturer indicates that the titroprocessor 636 is capable
of detecting equivalence points which cannot be recognized
visually as points of inflection in the titration curve path.
Differences between points of inflection and equivalence points
otherwise producing erroneous results are corrected for the most
part in the system.

Examples communicated by the manufacturer show that simultaneous
determination is still possible where equivalence points differ
by 2.5 to 3 pH units. This corresponds to just as many pK units
or the factor 300 to 1,000 in the K_A values. The performance
limits of the Titroprozessor 636 for simultaneous determination
appear to have been reached here.

Fig. 7 shows the Titroprozessor 636 with its propellant analysis
setup. For titration, the apparatus incorporates 2 motor piston
burettes of the Dosimat 635 type and a motor piston burette of
the type Dosimat 665 (with integrated microprocessor) as well as
a magnetic stirrer with sample container and holder for indicator
electrode. The three motor piston burettes allow freely selecta-
ble addition of measurement solutions (for example 0.5 N or 0.05
N KOH, 1 N NH_4NO_3 solution) and the dosage of auxiliary sub-
stances (for example acetone or formaldehyde solution).

A combined pH glass electrode ("single-rod glass electrode")
with a U glass membrane is used as an indicator.

The Titroprozessor 636 is controlled by cards. The cards are used
for operation and calculation modes and programmed by "rubbing
on" square black code markings.

5.5   Propellant analyses

5.5.1 NOS-365

In the case of the propellant NOS-365, it can be seen from
Section 5.4 and Table 11 that the simultaneous titration of the
components hydroxylammonium nitrate (HAN) and isopropylammonium
nitrate (IPAN) is possible with strong bases without difficulty.
This is confirmed by the titration curve printed out by the
titroprocessor in Fig. 8. The final titration point (1) of the
first component determined (HAN) is clearly prominent as a point
of inflection, as the K_A values of HAN and IPAN differ by the
factor $5.3 \cdot 10^4$. The final point of the IPAN determination (2)
is, however, difficult to recognize without additional help,
which is due to the high alkaline value of the primary amine.
Fig. 8.1, which shows the 1st derivative of the titration curve
from Fig. 8, makes this clear. In the 1st derivative, the turning
points appear as extreme values (max. or min.). The point of
equivalence (2) is now only recognizable as the crossing point of
two almost straight curve sections. Therefore, the accuracy
obtainable through titration with HAN should doubtlessly not be
expected from the IPAN determination.

The influence of derivative formation can be seen from Fig. 9:

With hydroxylamine, acetone forms acetoxim, and the final point
(1) in the determination of HAN is shifted into the acid range.
The change in pH in the equivalence range is in fact so great
that a chemical determination of the final point with color indi-
cator, e.g. methyl red, could be possible. The quotient from the

corresponding K_A values amounts to $1.4 \cdot 10^9$. This is the highest value which can be calculated from Table 11 at all. As can be seen from Fig. 9.1, equivalence point (2), the formation of derivate changes nothing for the determination of IPAN.

Figs. 10 and 10.1 document the simultaneous titration of 3 substances, i.e. HAN, IPAN and AN (ammonium nitrate). The final titration points must be drawn apart from each other through a two-time derivative formation (formation of acetoxim and hexamethylene tetramine through successive additions of acetone or formaldehyde solution accordingly). The quotients of the K_A values are $1.4 \cdot 10^4$ for the separation of HAN and AN and $1.0 \cdot 10^5$ for the separation of AN and IPAN (Table 11). The quotients are sufficiently large for the separations. As the quantity of AN is only low in the sample (generally below 0.5 %/wt.), it must be enlarged by adding a known quantity of ammonium nitrate to make separation possible.

With this method, the real AN content of the propellant is calculated as a difference in figures having practically the same magnitude. In such cases the accuracy attainable is only moderate. On the other hand, the determination of substances present in small concentrations only (example: less than 1 %/wt.) with less accuracy is sufficient.

5.5.2 LP 1845 and LP 1846

The LP 1845, which can be considered as a successor of NOS-365 (compare Section 5.1) contains, as correspondingly given in Fig. 6, 63 %/wt. HAN, 20 %/wt. TEAN and 17 %/wt. water.

In connection with stability tests on LP 1845, the question arose as to whether the propellant contains free acids or free bases. Simple pH measurement is less informative as the propellant mixture acts as a buffer. We therefore tried to recognize and

determine the free acid (nitric acid) possibly present in the propellant by potentiometric titration. Fig. 11 shows the titration tests with 0.05 N potassium hydroxide solution. The point of inflection of the titration curve is identified by the microprocessor as the equivalence point (1) with a flat but clear maximum in the 1st derivative.
The content of free nitric acid was determined at 0.31 %/wt.; a value which appears to be rational.

Titration curves obtained during a simulation titration of HAN and TEAN are reproduced in Figs. 12 and 12.1. The separation of HAN and TEAN by simple substitution titration is not possible as the quotient of the K_A values is only $6.5 \cdot 10^1$. After the formation of acetoxim, the K_A quotient reaches the value $10.6 \cdot 10^6$, and separation is possible without further difficulty. The final point of TEAN titration is also well indicated as triethanolamine – contrary to isopropylamine – belongs to the weak amine bases. The titration curve according to Fig. 12 therefore represents the typical example of a simultaneous titration process. This is especially confirmed by the sharp max. values in Fig. 12.1.

Opposed to this, the simultaneous titration of TEAN and AN is not possible. In the separation of AN (after the formation of hexamethylene tetramine nitrate) and TEAN, the K_A quotient only reaches the value of $1.3 \cdot 10^2$ and, without the formation of derivatives, only as much as $3.4 \cdot 10^1$.

The increase in the quantity of ammonium nitrate in the sample caused the inflection points to appear in the titration curve. The inflection points did not agree with the equivalence points. The differences once more depend on the quantity of ammonium nitrate in the sample. Corrections are complicated and uncertain. They are therefore not taken into consideration.

It was found that AN can be determined through the known process of ammoniac distillation from a sample made alkaline. The method

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works because triethanolamine is not volatile with water steam.
Hydroxylamine can be oxidized quantitatively to dinitrogen oxide
(N_2O) in a sample with Fehling's solution (Cu^{2+}-tartrate complex
in alkaline solution). No ammoniac as by-product is produced
in the process of oxidation here. We carry out distillation of
the ammonia in the Ströhlein apparatus, which was originally
designed for the determination of nitrogen in steels.

Figs. 13 and 14 show the Ströhlein water still. Steam is
generated in an electric boiler, conducted through a distillation
flask after drop separation, and is then condensed. The condensa-
tion product is absorbed by dilute boric acid in the old-
fashioned Volhard receiver. Finally, ammonia is titrated with
hydrochloric acid.
With this distillation method, it is possible to determine 0.1 %
wt. AN reliably.
The ammonium nitrate and the free nitric acid are only present in
small amounts, and the corresponding analytical data are needed
for correction purposes. The analytical methods were therefore
carefully cross-checked by adding known amounts of ammonium ni-
trate or nitric acid respectively to a sample of the propellant.
The water content of liquid propellants on the basis of HAN
according to Fig. 6 can be determined directly by Karl Fischer
titration. This method requires a special unit, as the Titropro-
zessor 636 is not suited for this. The presence of amines and
particularly the reductively acting hydroxylamine may lead to
disturbances. Such disturbances can be avoided if the Work Speci-
fications recommended by Messrs. Riedel - de Haen are followed
/21/.

5.6   Accuracy of the analytic determinations

If, in the chemical analysis of the quantity X (e.g. the content
of HAN in %/wt.), n individual tests are carried out, the most
probable value is the arithmetical mean $\overline{X}$ (X transverse):

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$$\overline{X} = \sum X/n \tag{17}$$

As a measure for the scattering of the individual values, the standard deviation s (also sigma - 1) is most frequently used /22/, /23/:

$$s = \sqrt{\frac{(X - \overline{X})^2}{n - 1}} = \sqrt{\frac{\sum X^2 - (\sum X)^2/n}{n - 1}} \tag{18}$$

$\overline{X}$ and s are given in the same unit, e.g. in mol/kg or frequently in percentage by weight (%/wt.) in chemical analysis methods. The measurements are especially accurate or inaccurate where s is small and $\overline{X}$ large or vice versa. To determine the accuracy of analysis, therefore, both values must be communicated. This means that the variation coefficient V is an instructive parameter for measurement error:

$$V = s \cdot 100/\overline{X} \tag{19}$$

The variation coeficient is given in relative percent (%).

In Table 12, the statistical quantities $\overline{X}$, s, V and n have been drawn up for analysis of the propellants LP 1845 and LP 1846. The compounds HAN, TEAN, AN and HNO_3 were determined. Unfortunately it was not always feasible due to the amount of work involved to follow through a sufficiently large number n (column 5) for individual determinations. It can nevertheless be recognized that the major component HAN can be determined the most accurately. The variation coefficient V (column 4) is between 0.15 and 0.2 %, this being a good result for a simultaneous determination.

The determination of TEAN had less accurate results: V had the value 1 - 1.9 %. The reasons for this have already been mentioned in Section 5.5.2: the correction in respect of the AN content and a lower quantity in the mixture.

In the case of ammonium nitrate, the V values are at their worst:
13 - 27 %. This is principally due to the fact that determination
of AN is the most difficult individual measurement in the analy-
sis of propellants. However, the comparatively high relative
errors are tolerable at the low AN contents involved.
Free nitric acid is also only present in small quantities in pro-
pellants, but the determination is easier than in the case of
ammonium nitrate. The variation coefficient is correspondingly
between 3 and 11 %.

6.   Test results

6.1   The storage of LP 1846 in glass ampoules

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

The accelerated storage tests were carried out on the effects
of precious metals, metals, stainless steels and gun steels on LP
1846 in glass 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 3. The metals were added in the form of filings or powder -
not as compounds, such as e.g. salts. The time measured up to the
bursting of a glass ampoule is a parameter for the compatibility
of the propellant with the metal concerned. This is related to
the storage life of the original (non-contaminated) propellant
and given as the relative life term. This relative life term is
recorded 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 3. 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 and copper) by more
than 90 % to < 6 % of the life term.

The stainless steels tested also produce a considerable shorten-
ing in the storage life of the liquid propellant. Thus, the sto-
rage life of LP 1846 is reduced by 26 % to 74 % when in contact
with stainless steel, German Standard No. 1.4571, and to 3 % with
stainless steel, German Standard No. 1.4541. The basic material
17-4 PH, German Standard No. 1.4542, from which the probes for
the pressure transducers are made, reacts with LP 1846 and shor-
tens the storage life of the propellant to 23 %.

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

Several different plastomers and elastomers, listed and described
in Table 4, 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/plastic sample is compared

with the storage life of the pure propellant (100 %). The results
are listed and compared in Table 5.
From this table, it can be seen that certain plastics, such as
e.g. ethylene-propylene-diene copolymers (EPDM), ethylene-
propylene copolymers (EP) and Viton (FPM) reduce the life term of
the liquid propellants in the same way as stainless steels.

6.1.2   Stability of liquid propellant LP 1846 depending on
         pH value

As the pH value increases, hydroxylammonium nitrate (HAN) and
triethanolammonium nitrate (TEAN) are split, releasing the
amines. Within a specific range (pH = approx. 4), the propellant
mixture acts as a buffer.

The free hydroxylamine is less stable than its salts. For this
reason, we initially assumed that an excess of nitric acid ought
to increase the stability of the propellant. Nevertheless, in the
highly concentrated propellant mixture here involved (approx. 20
% water content), free nitric acid acts as an additional oxidi-
zing agent. Previously conducted DSC (differential scanning calo-
rimetry) tests on various batches of NOS-365 confirmed our suspi-
cion that stability, as a function of the pH value, has a maximum
limit. Samples of NOS-365, which had a very low pH value (pH < 1)
after careful partial dehydration, already disintegrated at 70 °C
(158 °F) during DSC. As the acid concentration decreased (pH >
1.9), the disintegration temperature increased to 187 °C (368.6
°F) (see Fig. 15).

Our test series with LP 1846 covered pH values ranging from 0.7
to 4.3.   The pH values of the test solutions were adjusted using
nitric acid or solid magnesium oxide. The use of the latter sub-
stance was found to be favorable due to the fact that Mg ions do
not influence the stability of the propellant within the wide
range of concentrations concerned. Furthermore, the addition of

MgO does not modify the oxidant/fuel ratio to any considerable extent. The use of free hydroxylamine as a pH adjustor would have influenced propellant concentration noticably.

The pH values were measured on propellant samples which had been diluted with water at a 1 : 1 ratio.

Our tests yielded the following results:

Storage duration of LP 1846 as depending on pH value:
Accelerated storage tests in glass ampoules at 90 °C (194 °F).

pH value at dilution 1:1	Decomposition time in days
0.71	60.5
0.88	67.6
1.21	78.0
1.50	83.5
1.86	84.2
2.09	86.8
2.33	85.9
2.68	86.2
3.00	84.5
3.25	83.4
3.46	82.6
3.65	81.8
3.85	81.2
4.29	80.1

Where stability depends on the pH value, a weakly noticable maximum, i.e. a stability optimum situated around pH = 2.4, is observed. The deviations in measurement value in the region of pH = 2.0 and pH = 2.6 are within measurement accuracy.

In the acid range at pH < 1.9, the storage life of the samples in the ampoules is rapidly shortened. This drops from 86 to 60 days at 90 °C (194 °F). Within a weaker acidic range, changes in the pH value only influence storage life to a minor extent: at a pH value of 4.3, this life period still amounts to 80 days.

6.1.3   The influence of metal ions on the chemical stability of LP 1846

All liquid propellants based on HAN react to impurities, especially to metal ions. The disadvantages of propellant decomposition have been pointed out in Section 1.

In this study, we examined the influence of metal ions, according to type and concentration, on the decomposition of the propellant LP 1846. The metal ions were applied - where possible in the form of nitrates - in concentrations between 0.5 and 100 ppm.

This meant that uncontrollable influences from further anions (e.g. chloride, sulfate) were thus eliminated. However, a number of metals were only available in the form of oxides, and had to be applied in this form. As an additional precautionary measure, we selected those metal ions with the lowest state of oxidation or, respectively, the highest stability.

As before, equal quantities of sample were first weighed at all times in these tests as well, as the generation of gas and the pressure increase rate depend on the quantitiy of substance supplying the gas.

Tables 13 and 14 give a survey of the relative decomposition times (in %) for the concentration range from 2 to 100 or 0.5 to 100 ppm respectively. The metal ions in the first column are listed to give the decreasing propellant storage life periods in the last column (metal ion concentration = 100 ppm). At the be-

ginning of the table, those ions are shown which do not influence
decomposition at all or only a very little up to a concentration
of 100 ppm. The ions at the end of the table increase decomposi-
tion the most. In the case of these ions, their action depends to
a high degree on their concentration.

Contrary to a large number of different ion types for which
concentrations of more than 10 ppm are necessary to obtain any
kind of measurement results at all, we can still expect, in the
case of iron, copper, vanadium and palladium ions, an influence
on the respective life terms at levels below 2 ppm. In addition
we measured these ions at concentrations of 0.5 and 1 ppm, the
results of which have been listed separately in Table 14 for the
obvious reason of clarity.

It can be recognized immediately that, in concentration ranges
below 10 ppm, palladium ions exert no influence whatever on the
decomposition of the propellant. Contrary to this, iron, copper
and vanadium ions still manifest a clear influence on its life
term at concentrations of 0.5 ppm. Consequently, these ions must
be kept out of all HAN-based propellants as far as absolutely
possible, as they are capable of shortening the life term of this
propellant type to a highly effective extent.

6.1.4   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.

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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 'stabili-
zers' 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 deri-
vates and substances reacting in a similar way under this aspect
/24/25/, 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 decom-
position by avoiding metal ions. Such a demand can only be real-
ized with difficulty when operating with HAN under practical or
near-practical conditions. Therefore, the effects of metal ions
on the HAN must be suppressed 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, e.g. the transfer of metal ions into very stable com-
plexes /26/. However, in practice, this is restricted due to the
fact that most complex compounds do not possess a sufficient sta-
bility. 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 removal of the disturbing metal
ions could also be achieved via carrying down with precipitation
reagents. If it is possible to demonstrate a reduction in decom-
position, it would consequently be a worthwhile enterprise to
pursue this line. This is why the attempt was made to diminish

the decomposition of copper- and iron-contaminated LP 1846 using
complex-forming substances (Tab. 15). 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. In
both of these measurement ranges, the results showed no stabili-
zing influence on the LP. These tests were then continued with
other test substances, as well as at other concentrations.

From the reaction mechanisms involved in propellant decomposition
discussed in Section 3. above, it can be seen that pure hydroxyl
ammonium nitrate too is subject to a permanent decomposition
(Fig. 1, Eq. 2). In this case, due to a disproportionating reac-
tion, inert dinitrogen oxide, N_2O, is formed. Nitrous acid, HNO_2,
which is formed in a secondary reaction, is absorbed by the large
excess of HAN, through which dinitrogen oxide is also produced. A
stabilizer for neutralizing the nitrous acid and/or the N_2O_3 is
therefore not necessary.

Metal ions, such as those of Fe, Cu and V, accelerate the forma-
tion of the intermediate compound dihydroxylamine (Fig. 1
Equation 6). All measures for stabilization must therefore be
directed at a reduction of the metal ion concentration. It has
been our aim to suppress decomposition through complexing the
metal ions in the case of the substances now tested.
Unfortunately, most of the metal ion complexes are not suffici-
ently stable where the pH values of the HAN-based propellants are
concerned (pH = approx. 2). On account of the pH-dependent disso-
ciation equilibrium of these complexes, metal ions are left over
in sufficient quantity to catalyze the decomposition of the hyd-
roxylammonium nitrate.

Among the potential stabilizers tested we also found commercially

available products properly marketed as water softeners. In
actual fact, these substances form heavy metal complexes which
are also stable in acid solutions. No details are available at
the present time on the equilibrium constants of complex forma-
tion which, by their very nature, possess different values for
each type of ion. The equilibrium constants will have to be de-
termined for substances which have demonstrated their efficacy in
our tests. Table 16 gives a list of such complexing agents and
with details on their composition and the companies supplying
them. Their effect on liquid propellants containing Fe ions is
shown in Tables 17 and 18. A number of chelating substances are
capable of forming a number of chelate bonds, so that the mol
numbers of metal ions and complexing agents with ratios of 1 : 1
and 1 : 10 were selected for our tests. Whereas the decomposition
time of a sample containing 10 ppm Fe ions and no other additives
took 17.4 days, a number of phosphonates prolonged the decomposi-
tion times to a manifest extent. The increases in storage life
are even more significant at a molar ratio of 1 : 10.

From Table 17, it can be seen that the organic polyaminophospho-
nic acids show a significant stabilization effect.

Through the addition of Turpinal D 2, the life of the propellant
was increased from 14.4 (= 100 %) to 42.5 days, i.e. by a factor
of 2.4. The corresponding times were 47.4 days (factor: 2.7) for
Dequest 2041, and 39 days (factor: 2.2) for (HCl-free) Dequest
2060 S. Dequest 2060 S is supplied with 16 % free hydrochloric
acid, and the preparation even shortens the life term. Through
purification of the acidified Dequest 2060 S, an HCl-free product
with stabilizing properties could be obtained. The remaining sub-
stances tested as shown in Table 17 revealed either no or only
slightly stabilizing effects (e.g. 1-nitroso-2-naphthol, Titri-
plex IV = CDTA, tributyl phosphate). According to our measure-
ments, alpha-alpha'-dipyridyl, which is quoted in relevant lite-
rature, has no complexing effect as regards iron ions.

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The influence of stabilizers on propellant samples with a higher
content of metal ions (100 ppm copper or iron ions respectively)
is shown in <u>Table 18</u>. The ratio between metal ions and stabilizer
molecules was 1 : 1.

Only a slightly stabilizing effect was measured in the propellant
samples mixed with copper ions, such as e.g. with quinoline-2-
carboxylic acid (factor: 1.3) and with Turpinal D 2 (factor:
1.2).
As a stabilizer, Dequest 2041 is dominant in the presence of iron
ions, increasing the life term of the propellant samples by a
factor of 3.8 times. Turpinal D 2 showed approximately the same
stabilizing effect as at a content of 10 ppm (factor: 1.7).
At higher concentrations, a number of stabilizers caused turbidi-
ty in the propellant liquid. Segregation of this kind may result
in the formation of sludge or to two different phases.
In some cases, the stabilizers produced characteristically co-
lored complexes with the metal ions contained in the propellant.
This behavior could be used as a simple test for impurities.

6.1.5   The collective influence of copper- and iron
ions (cumulation effect)

Our tests were also aimed at establishing what influence the mu-
tual presence of Cu and Fe ions have on the rate of decomposi-
tion. Corresponding ampoule tests were carried out with the fol-
lowing three types of solution:

I. Pure propellant without the addition of metal ions (Stan-
    dard);

II. Propellant with the addition of Fe or Cu ions;

III. Propellant with the addition of Fe and Cu ions at different
     ratios.

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The results are shown in <u>Table 19</u> as a dependence of the life
time of LP 1846 on the type and concentration of the ion addi-
tives. It is thus possible, from this table, to draw the follow-
ing conclusions: at higher concentrations, e.g. 10 ppm Fe and 10
ppm Cu, the influence of the Cu ions is overlapped by the pro-
nounced influence of the Fe ions. A certain additive property of
these effects can only be demonstrated at low concentrations. An
increase of decomposition through ion mixing ("cumulation ef-
fect") cannot be recognized.

6.2   <u>Continuous observation of LP 1846 decomposition by</u>
         <u>measuring the rise in pressure</u>

6.2.1   <u>Pressure measurement to determine the influence of</u>
         <u>metal ions on the storage life of LP-1846</u>

In the pressure measurements, as described in detail in Section
4.2., metal ions differing in type and concentration were added
to the pure LP solution in a way similar to that practiced in the
ampoule tests. After storage of these samples at a test tempera-
ture of 90 °C (194 °F), the pressure / time curves were measured
and recorded. The storage tests were discontinued when a pressure
of 4 bar was reached. The curves were compared with those ob-
tained using pure liquid propellant as a reference substance. Un-
der the test conditions applied (temperature, type and concentra-
tion of metal ion), the time up to when the final pressure (4
bar) is reached may thus be defined as the "lifetime" of the pro-
pellant.
After termination of the test, the content of HAN, TEAN, NH_4NO_3
and HNO_3 in the sample residue were determined potentiometrically
(comp. Section 5).

An increase in storage temperature from 90 °C to 95 °C (194 to
203 °F) was not found to be useful. In this case, spontaneous,

uncontrollable decompositions occurred in those samples which, for example, contained only the less active Ni^{++} and Co^{++} ions. Pressures of over 50 bar resulting in destruction of the pressure sensors were measured.

In a number of samples, a minor pressure decrease of approx. 0.1 bar was found over the first 24 hours, only to even out over the following 24 hours. The samples concerned either contained very low concentrations of metal ions (less than 1 ppm) or substances not effective in decomposition. We suspect that this is due to oxygen initially enclosed in the containers together with the samples being used up through reaction with the propellant, only to be replaced later on by the gases produced in decomposition. This phenomenon was therefore not taken into consideration in the graphic evaluation of the measurement data.

For the measurements, we made use of experience gained from the ampoule trials (Tab. 13). Initially, we only tested the most effective ions, and these only in low concentration ranges. Apart from the reference substance (pure propellant), we also tested a few selected, less effective ions due to the fact that the metals here concerned occur frequently, for example as alloying components in stainless steel.

Table 20 provides a survey of the measurement values obtained with the ions of V, Fe and Cu at a concentration of 10 ppm. As standard, the measurement results recorded with pure propellant tested under exactly the same conditions were included. The marked influence of the three types of ion named is recognizable by their shortening the lifetime of the sample and causing a rapid increase in pressure.

In the partial decomposition encountered, ammonium nitrate and nitric acid can be demonstrated and quantitatively determined as stable final products. The pressure build-up is principally produced by the decomposition of approx. 5 % HAN. The decrease in

the TEAN component is low up to a pressure of 4 bar. A series of
measurement values obtained with V, Cu and Fe ions at concentra-
tions ranging from 0 to 10 ppm is given in the Tables 21, 22 and
23. The storage duration shows a clear dependence on the concen-
tration of the different ions. Even concentrations as low as 1
ppm exert a considerable influence on the life time. No form of
dependence can be derived, on the other hand, from the relation
between the composition of the sample residue (remaining solu-
tion) and the concentration of the metal ions applied.

Fig. 16 gives the influence of metal ion concentration on
lifetime. It can be recognized that the metal ions listed shorten
the life of a propellant significantly already at a concentration
of 1 ppm. Copper ions here encourage decomposition least of all,
whereas the iron and vanadium ions agree with each other in their
- considerable - effects.

From Fig. 16 we are thus able to conclude that, primarily, the
highest obtainable degree of purity is decisive for the optimal
stability of a propellant.

Fig. 17 gives the pressure/time curves of several ions having a
more pronounced or a weaker effect. In these tests, the ion con-
centration was 10 ppm through.ut. Here, too, pure propellant was
used to obtain reference values for comparison.

From the uniform progression of the pressure/time curves, we are
able to conclude that the sample residues (remaining solutions)
ought also to have compositions agreeing with each other: in
spite of this, we have not been able to detect dependences of
this type up till now. From information given in the relevant
literature /3/, we may assume by way of an explanation that
different metal ions are the source of different mechanisms and,
consequently, different reaction products as well. The differing
contents in ammonium nitrate attracted our attention when assess-
ing the analysis values. We found - to the deficit of the HAN

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concentration - more than 3 % ammonium nitrate, particularly when Cu ions are present (comp. Table 20).

6.2.2 The influence of stabilizers on the storage life of LP 1846

Tests on stabilizing additives, especially in the presence of iron ions, were already reported on in Section 6.1.4 (tests with glass ampoules). Dequest 2041, the most effective additive found in these tests, was then chosen for stability tests with continuous measurement of the pressure rise. As with the tests in glass ampoules, the following samples were examined:

I. Original LP 1846 propellant by itself as a reference substance;

II. Propellant with added iron ions at a concentration of 10 ppm;

III. Propellant with added iron ions (10 ppm) plus Dequest 2041; mol ratio Fe^{2+} : Dequest 2041 = 1 : 10.

The pressure/time curves up to a final pressure of 4 bar are given in Fig. 18. The stabilizing effect of Dequest 2041 can be seen quite clearly from these curves. Whereas, in the samples prepared according to method II above, the final pressure of 4 bar was already attained after 8 days, the type III. samples did not reach this pressure until after 31 days. In the case of the fresh pure propellant (reference), this pressure was not reached until after 42 days.

The values of quantitative chemical analysis from the test series according to Items I. through III. above have been compiled in Table 24. These values confirm the insights gained from the tests conducted with glass ampoules (compare Section 6.1.4): nitric acid and ammonium nitrate are formed upon disintegration of the propellant during long-term storage at 90 °C (194 °F). The quan-

tity of hydroxylammonium nitrate (HAN) contained and the pH value
both decrease.

These initial results are encouraging, although we must take the
fact into consideration, however, that the life term of pure pro-
pellant is considerably greater than that of samples to which
metal ions (i.e. impurities) and then stabilizers to complex them
were added. In spite of this, the objective of providing propel-
lants with an added protection against decomposition due to impu-
rities should still be pursued further.

In assessing the value of stabilizers, E. Freedman /27/ is of the
opinion that a storage temperature of 90 °C (194 °F) shows the
effect of these stabilizers in a disproportionately bad light.
This author feels that lower storage temperatures of e.g. 65 °C
(149 °F) would be far more suitable and realistic.

7.   Summary

In the "HAN-based" liquid propellants, hydroxylammonium nitrate
(HAN) is the substance most capable of reaction, decomposing into
gaseous compounds, particularly in the presence of specific impu-
rities. This property thus formed the starting point of our stu-
dies on the stability of HAN-based propellants.

A long-term storage at high temperatures in pressure containers
was therefore a particularly suitable method for testing the
stability of these liquid propellants.

Two methods are described:

- Storage in glass ampoules, and

- Storage in glass containers with connected pressure sensors.

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The time up to when a specified pressure is reached provides sensitive parameters for the assessment of impurities.
Simultaneous potentiometric titration methods were worked out for a quantitative determination of the concentration of components in fresh propellant as well as of decomposition products.

Three different types of reaction could be distinguished where the liquid propellant LP 1846 came into contact with pure metals:

I. A number of metals such as antimony, rhenium, iron and copper, cause the propellant to decompose in a very energetic manner, whereby these metals are dissolved more or less rapidly;

II. Other metals such as zink and manganese are dissolved by the propellant without influencing its lifetime;

III. Finally, we find metals such as gold, silver and tantalum which are neither attacked nor reduce stability. These metals are suitable as materials coming into contact with the propellant.

A number of steel alloys, such as stainless (high-quality) steel, produce a considerable decomposition. Thus, the propellant showed a particularly low stability in the presence of two gunmetals.

Of the sealing materials examined, only polytetrafluoroethylene (PTFE) and polychlorotrifluoroethylene (PCTFE) remained consistently stable and without influence on the stability of the propellant. Other sealing materials were themselves subject to severe attack and accelerated the decomposition of the propellant to an extent equalling that of steel alloys.

Metal ions entering the propellant as impurities or via the corrosion of contact materials also exert a more or less important influence on the propellant's stability. Apart from the well-known, very prominent decomposing effect of copper and iron ions,

a highly marked effect of this type could also be recorded for vanadium ions. A restriction of stability could already be recorded for vanadium compounds even at concentrations of less than 0.5 ppm.
At contents of less than 10 ppm, most other metal ions only showed a slight effect.

The stability of the liquid propellant LP 1846 was influenced by pH value in such a way that a maximum stability was reached within a pH range between 1.9 to 2.7. The optimum pH value is at 2.1 (at all times measured at a ratio of 1 : 1 with samples diluted in water).

Many organic compounds are capable of forming chelate compounds with metal ions, and we should thus attempt to make metal ions incapable of causing any damage in this way.

As, in the case of chelate formations, we are dealing with equilibrium reactions, there is often a residual content of metal ions present in the propellant, which reduces its stability. We could demonstrate a clear stabilization effect in the case of a number of aminophosphonic acids. Through the addition of the phosphonic acid Dequest 2041, it was possible to increase the lifetime of an LP 1846 sample containing 10 ppm iron ions and stored at a temperature of 90 °C (194 °F) from 17 to 47 days. Although this effect does not appear to be sufficient for practical purposes yet, it is an encouraging motivation to carry on further research.

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9. Annex (Figures and Tables)

9.1. Figures

Fig. 1:   The reaction mechanisms occurring in the decomposition of HAN and IPAN as found in the monergol NOS-365.

Fig. 2:   The decomposition products of the liquid monergol LP 1846.

Fig. 3:   Test arrangement for pressure measurements on liquid propellants (all dimensions are metric).

Fig. 4:   Measurement of longitudinal and transverse expansion as depending on internal pressure using strain gauges on glass ampoules.

Fig. 5:   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); T in K

Fig. 6:   Composition of liquid propellants.

Fig. 7:   The Metrohm Titroprozessor 636 with the propellant analysis section.

Fig. 8:   Analysis of NOS-365:
Simultaneous determination of HAN and IPAN by substitution titration: titration curve.

Fig. 8.1:   Analysis of NOS-365:
Simultaneous determination of HAN and IPAN by substitution titration: 1st derivative of titration curve.

Fig. 9:   Analysis of NOS-365:
Simultaneous determination of HAN and IPAN by substitution titration after formation of acetoxim by acetone additive: titration curve.

Fig. 9.1:   Analysis of NOS-365:
Simultaneous determination of HAN and IPAN by substitution titration after formation of acetoxim by acetone additive: 1st derivative.

Fig. 10:   Analysis of NOS-365:
Simultaneous determination of HAN, IPAN and AN by substitution titration:
Here: determination of HAN after formation of acetoxim by the addition of acetone.

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Fig. 10.1: Analysis of NOS-365: Simultaneous determination of
HAN, IPAN and AN by substitution titration: titration
curve (top) and 1st derivative (bottom).
Here: 1) Determination of AN after the addition of
ammonium nitrate at a known quantity and the
addition of formaldehyde (formation of
hexamethylene tetramine)
2) Determination of IPAN.

Fig. 11: Analysis of LP 1845: Determination of free nitric
acids: titration curve (top) and 1st derivative
(bottom).

Fig. 12: Analysis of LP 1845: Simultaneous determination of HAN
and TEAN by substitution titration: Titration curve.
Here: 1) Determination of HAN after acetoxim formation
by the addition of acetone
2) Determination of TEAN.

Fig. 12.1: Analysis of LP 1845: Simultaneous determination of HAN
and TEAN by substitution titration: 1st derivative.
Here: 1) Determination of HAN after acetoxim formation
by the addition of acetone
2) Determination of TEAN.

Fig. 13: Steam distillation unit after Ströhlein.

Fig. 14: Diagrammatic representation of the steam distillation
unit:
(1) Inlet connection for the sample, (2) Boiler inlet
tube, (3) Electric boiler, (4) Drop separator, (5)
Collector flask, (6) Spiral condenser, (7) Distilling
flask, (8) Receiver.

Fig. 15: DSC spectra of dehydrated NOS-365 as depending on the
pH value. Weight of sample 15 mg; heating rate: 6 °C
(10.8 °F) per minute.

Fig. 16: Storage time of LP 1846 as depending on metal ion
concentration (V, Cu, Fe). Accelerated storage tests
in pressure testing apparatus at 90 °C. Final
pressure: 4 bar.

Fig. 17: Pressure/time curves of contaminated LP 1846. Metal
ion concentration 10 ppm. Accelerated storage tests in
pressure testing apparatus at 90 °C.

Fig. 18: Pressure/time curves of LP 1846: original;
contaminated (10 ppm Fe^{2+}); contaminated with 10 ppm
Fe^{2+} and stabilized with Dequest 2041 (Fe/Dequest =
1/10). Accelerated storage tests in pressure testing
apparatus at 90 °C (194 °F).

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9.2   Tables

Table 1:   Analysis values for monergols containing HAN.

Table 2:   The composition of stainless steels.

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

Table 4:   The selection of suitable sealing materials.

Table 5:   The influence of sealing materials on the chemical
                stability of LP 1846. Accelerated storage test in
                glass ampoules at 90 °C (194 °F).

Table 6:   The permeation coefficients P of sintered PTFE
                (Hostaflon, manufactured by Hoechst AG, FR Germany) at
                room temperature in accordance with German Standard
                DIN 53380. Units of P as in Table 7

Table 7:   The temperature dependency of the permeation
                coefficients P of PTFE (Hostaflon) with Helium.

Table 8:   The temperature dependency of the permeation
                coefficients P of amorphous PCTFE (Voltalef 300)
                for a number of gases. Permeation coefficient $\times 10^{10}$.

Table 9:   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; $r_1 = 4$ mm; $d = 2$ mm; $A = 0.63$ cm^2) of the
                testing apparatus.

Table 10:   Gas pressure p (in bar) in glass containers at 25 °C
                (77 °F) as depending on time t (in days); T_c =
                measurement temperature in °C.

Table 11:   Dissociation constants K_A as well as relevant
                pK_A and pK_B values of several propellant components in
                aqueous solution at 20 °C.

Table 12:   Characteristics $\overline{X}$, s, V and n for the statistical
                evaluation of propellant analyses.

Table 13:   Comparison of the relative decomposition times of LP
                1846. Accelerated storage tests in glass ampoules at
                90 °C (194 °F). Metal ion concentrations of 2, 5, 10
                and 100 ppm.

$$2 \ NH_2OH \cdot HNO_3 \longrightarrow NH(OH)_2 + NH_4NO_3 + HNO_3 \qquad (1)$$

$$2 \ NH(OH)_2 \longrightarrow N_2O + H_2O \qquad (2)$$

$$2 \ NH(OH)_2 + HNO_3 \longrightarrow NH_2OH \cdot HNO_3 + HNO_2 \qquad (3)$$

$$NH_2OH \cdot HNO_3 + HNO_2 \longrightarrow N_2O + 2 \ H_2O + HNO_3 \qquad (4)$$

$$NH_4NO_3 + HNO_2 \longrightarrow N_2 + 2 \ H_2O + HNO_3 \qquad (5)$$

$$NH_2OH \cdot HNO_3 + 2 \ Fe(NO_3)_3 + H_2O \longrightarrow$$
$$NH(OH)_2 + 3 \ HNO_3 + 2 \ Fe(NO_3)_2 \qquad (6)$$

$$3 \ Fe^{2+} + NO_3^- + 4 \ H^+ \longrightarrow 3 \ Fe^{3+} + NO + 2 \ H_2O \qquad (7)$$

$$2 \ Fe(NO_3)_2 + NH_2OH \cdot 2 \ HNO_3 \longrightarrow$$
$$NH_4NO_3 + 2 \ Fe(NO_3)_3 + H_2O \qquad (8)$$

$$(CH_3)_2CH-NH_2 \cdot HNO_3 \xrightarrow[- \ HNO_3]{+ \ N_2O_3} (CH_3)_2CH-NH_2-NO)^+ + NO_2^-$$

$$\xrightarrow{- \ HNO_2} (CH_3)_2CH-NH-NO \longrightarrow (CH_3)_2CH-N=N-OH \qquad (9)$$

$$\xrightarrow[- \ H_2O]{+ \ H^+} (CH_3)_2CH-N^+ \equiv N \mid \xrightarrow[- \ N_2, -H^+]{+ \ H_2O} (CH_3)_2CH-OH + CH_2=CH(CH_3)$$

$$\xrightarrow[- \ H_2O]{+ \ Ox} (CH_3)_2C=O \xrightarrow{+ \ Ox} CH_3-COOH + HCOOH \xrightarrow[- \ H_2O]{+ \ Ox} CO_2$$

Fig. 1: The reaction mechanisms occurring in the decomposition of HAN and IPAN as found in the monergol NOS-365.

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Fig. 2: The decomposition products of the liquid monergol LP 1846.

Test arrangement for pressure measure=
ments on liquid propellants

Fig. 3: Test arrangement for pressure measurements on liquid
propellants (all dimensions are metric).
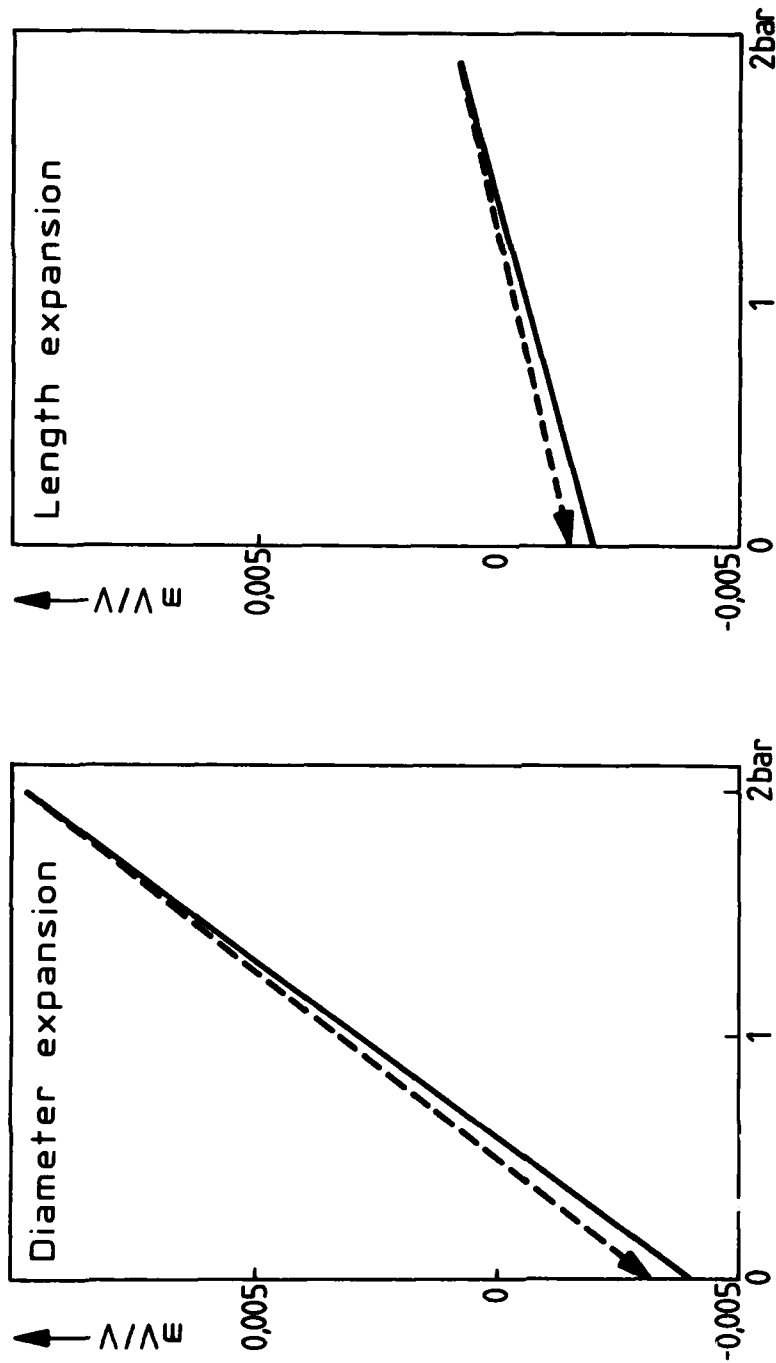
Fig. 4: Measurement of longitudinal and transverse expansion as depending on internal pressure using strain gauges on glass ampoules.
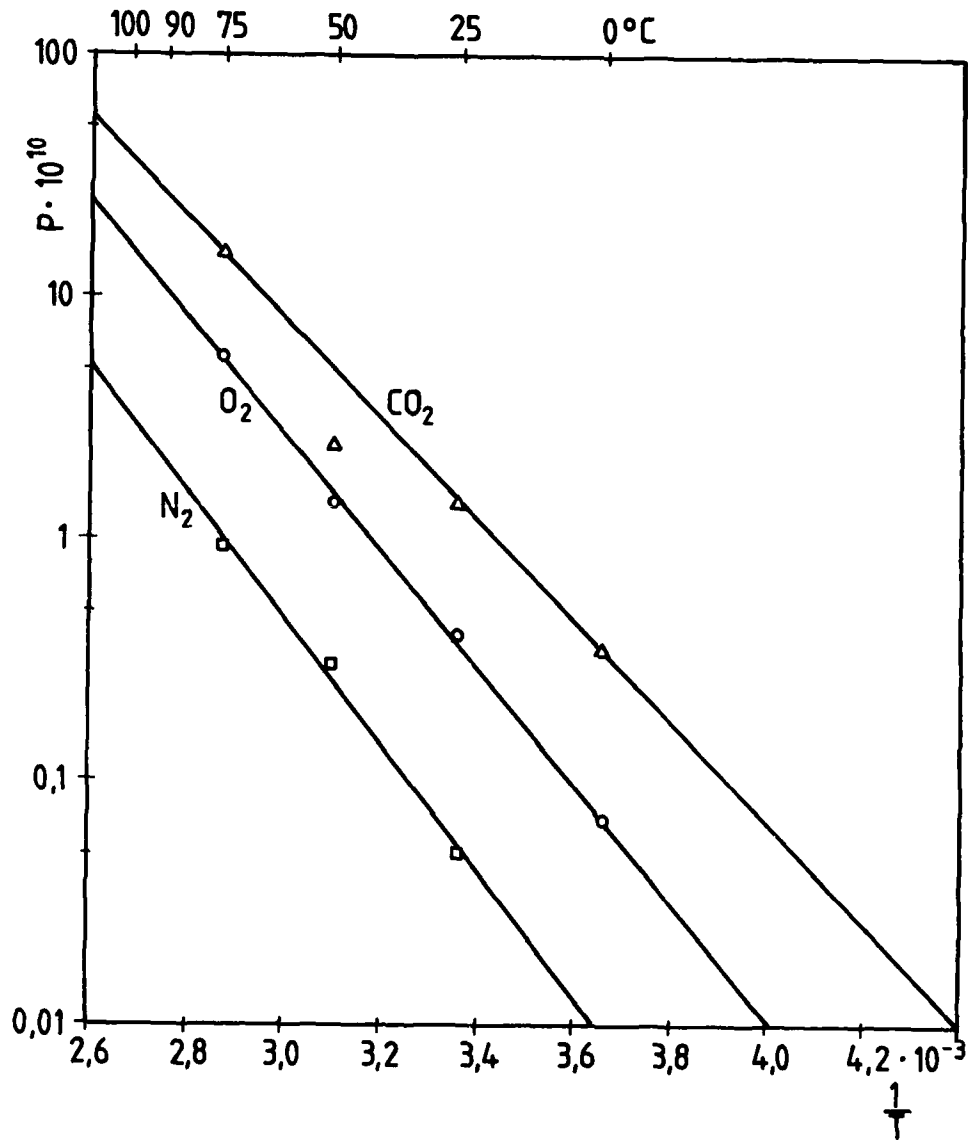
Fig. 5: Exponential temperature dependency of the permeation coefficients P of PCTFE (Voltalef 300) for N_2, O_2 and CO_2. P in cm · mm /s · (cm Hg); T in K

Code name	Combustion mat. Symbol [wt.%]	HAN [wt.%]	Water [wt.%]	Oxygen balance [%]	Impulse [J/g]	Flame temperat. [K]
LP-1776	TMAN 19,3	60,8	19,9	0,03	960,7	2600
1781	EOAN 32,5	50,3	17,2	- 0,0	929,6	2560
1812	TEN 13,6	67,5	18,9	- 0,04	959,8	2670
1814	TEN 13,2	65,3	21,5	- 0,1	924,7	2500
1835	TEN 11,8	68,4	19,8	+ 3,25	885,7	2410
1845	TEAN 20,0	63,2	16,8	- 0,05	982,3	2730
1846	TEAN 19,2	60,8	20,0	- 0,01	934,5	2570
1848	TEAN 14,5	66,3	19,2	+ 6,78	820,7	2260

TMAN ... Trimethylammonium nitrate $(CH_3)_3 N \cdot HNO_3$

EOAN ... Ethanol ammonium nitrate $HOCH_2CH_2NH_2 \cdot HNO_3$

TEN ... Triethylammonium nitrate $(CH_3CH_3)_3 N \cdot HNO_3$

TEAN ... Triethanol ammonium nitrate $(HOCH_2CH_2)_3 N \cdot HNO_3$

Fig. 6: Composition of liquid propellants.

Fig. 7:   The Metrohm Titroprozessor 636 with the propellant
analysis section.

Fig. 8: Analysis of NOS-365:
Simultaneous determination of HAN and IPAN by
substitution titration: titration curve.

Fig. 8.1: Analysis of NOS-365:
Simultaneous determination of HAN and IPAN by
substitution titration: 1st derivative of titration
curve.

Fig. 9: Analysis of NOS-365:
Simultaneous determination of HAN and IPAN by
substitution titration after formation of acetoxim by
acetone additive: titration curve.

1.00ML/DIV V(START)/ML   0.000

82   1

175

18   2

ROUTINE #   201
222   PH(INIT) 1.326   V(TE)/ML 15.941
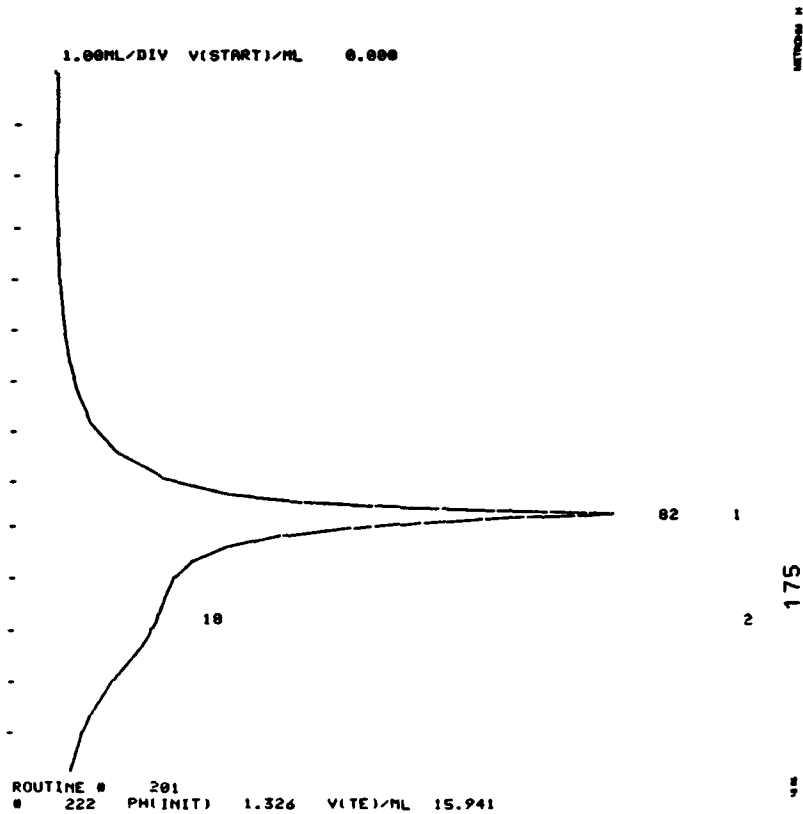
DATE   6.11.86   NAME J

BUR.2 V/ML	20.0	ROUTINE # 201
TEMP/C	18.0	REAGENT 0,5 n KOH wäßr. Titrisol
KINET D	8.0	TITER 1.000
MPD VAR	8.0	ELECTRODES 2 kombinierte Glaselektrode Metrohm, geeicht
START V/ML	0.000	
STOP PH	100.000	SAMPLE 712,8 mg NOS 365 + 10 ml Aceton
STOP V/ML	20.000	
STOP # EP	9.0	
PAUSE/S	0.0	
EP-CRIT	5.0	REMARKS
ADD V/ML	0.000	
EP-W LIM1	0.000	
PH LIM2	14.000	
0105		

Fig. 9.1: Analysis of NOS-365:
Simultaneous determination of HAN and IPAN by
substitution titration after formation of acetoxim by
acetone additive: 1st derivative.

Fig. 10: Analysis of NOS-365:
Simultaneous determination of HAN, IPAN and AN by
substitution titration:
Here: determination of HAN after formation of acetoxim
by the addition of acetone.

1.00ML/DIV V(START)/ML   0.000   PH

0 , 1 , 2 , 3 , 4 , 5 , 6 , 7 , 8 , 9 , 10 , 11 , 12 , 13 , 14

185

1

2
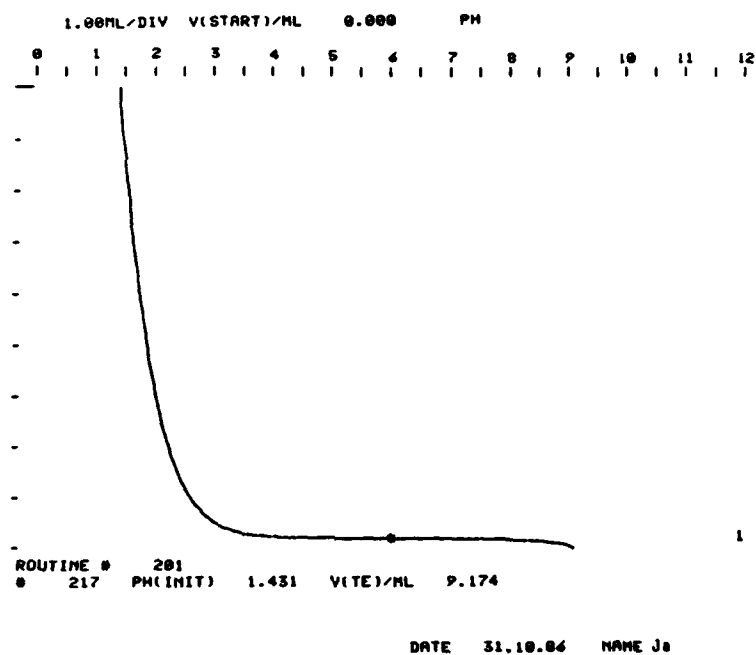
ROUTINE #   1
217   PH(INIT)   5.485   V(TE)/ML   5.868
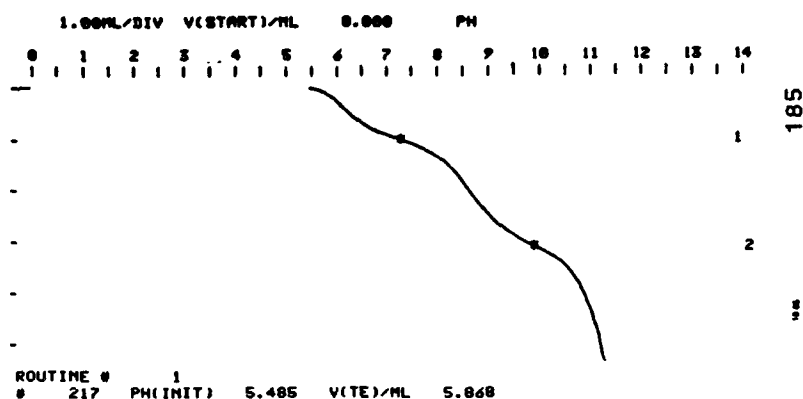
DATE   31.10.86   NAME Ja

BUR.2 V/ML   10.0   ROUTINE #   201
TEMP/C   25.0   REAGENT 0,5 n NaOH wäßr. Titrisol
KINET D   0.0   TITER   1,000
MPD   VAR   0.0   ELECTRODES 2 kombinierte Glaselktrode Metrohm
START V/ML   0.000
STOP PH   100.000   SAMPLE 722,6 mg NOS 365 + 10 ml Aceton (HAN-Best.)
STOP V/ML   10.000   + 5 ml Formaldehyd 37 %
STOP # EP   7.0   + 406,9 mg NH₄NO₃ Lsg. (=38,61 mg 100 %)
PAUSE/S   0.0
EP-CRIT   5.0   REMARKS
ADD V/ML   0.000
EP-W LIM1   0.000
PH   LIM2   14.000
0105

1.00ML/DIV V(START)/ML   0.000

49   1

41   2

ROUTINE #   1
217   PH(INIT)   5.485   V(TE)/ML   5.868

DATE   31.10.86   NAME Ja
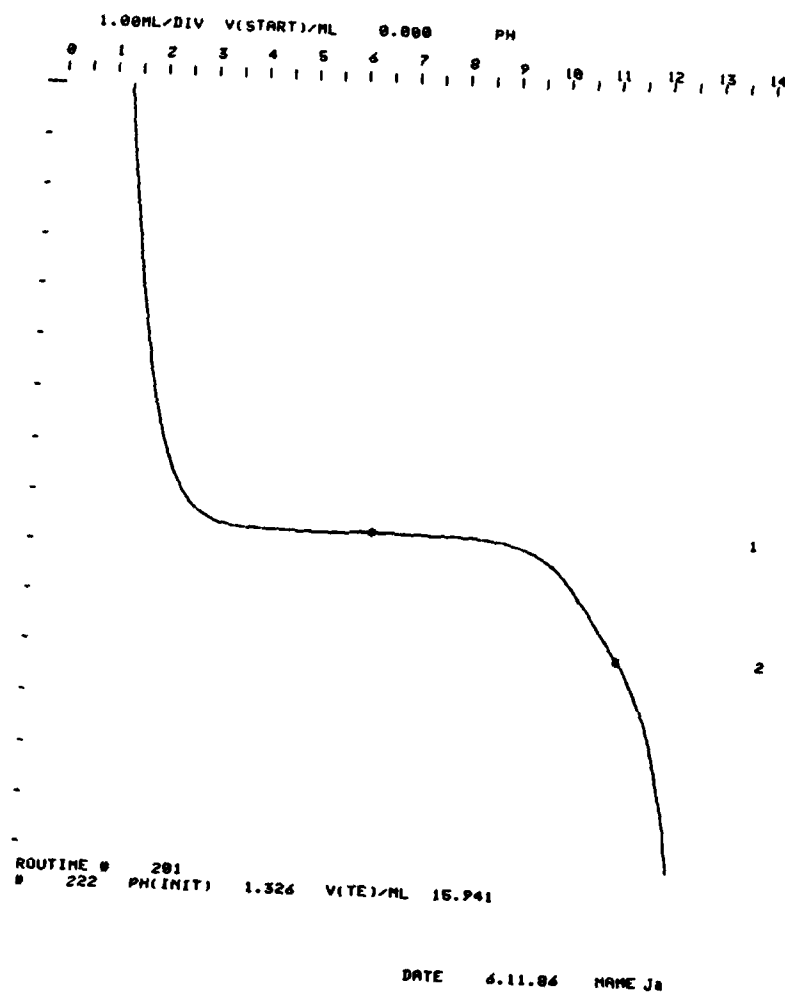
Fig. 10.1: Analysis of NOS-365: Simultaneous determination of
           HAN, IPAN and AN by substitution titration: titration
           curve (top) and 1st derivative (bottom).
           Here: 1) Determination of AN after the addition of
                    ammonium nitrate at a known quantity and the
                    addition of formaldehyde (formation of
                    hexamethylene tetramine)
                 2) Determination of IPAN.

0.50ML/DIV V(START)/ML   0.000   PH

0   1   2   3   4   5   6   7

ROUTINE #   201
24   PH(INIT) 2.757   V(TE)/ML   4.116
1 V/ML   1.651 PH(M)   3.361

DATE   10.11.86   NAME

0.50ML/DIV V(START)/ML   0.000

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ROUTINE #   201
242   PH(INIT) 2.757   V(TE)/ML   4.116
1 V/ML   1.651 PH(M)   3.361 â 5,20 mg HNO$_3$ ≙ 0,31 % HNO$_3$

DATE   10.11.86   NAME Ja

BUR.2 V/ML	10.0	ROUTINE #	201
TEMP/C	21.0	REAGENT 0,05 n NaOH waßr.	
KINET D	0.0	TITER 1,000	
MPD VAR	0.0	ELECTRODES 2 kombinierte Glaselektrode Metrohm,	
START V/ML	0.000		geeicht.
STOP PH	100.000	SAMPLE 1672,3 mg LP 1845, Thiokol	
STOP V/ML	10.000		
STOP # EP	9.0		
PAUSE/S	0.0		
EP-CRIT	5.0	REMARKS Säurebestimmung	
ADD V/ML	0.000		
EP-W LIM1	0.000		
PH LIM2	14.000		
0105			

Fig. 11: Analysis of LP 1845: Determination of free nitric acids: titration curve (top) and 1st derivative (bottom).

Fig. 12: Analysis of LP 1845: Simultaneous determination of HAN
and TEAN by substitution titration: Titration curve.
Here: 1) Determination of HAN after acetoxim formation
by the addition of acetone
2) Determination of TEAN.

1.00ML/DIV   V(START)/ML   0.000

PH(INIT)   1.270
1   V/ML   11.537   PH   5.102   â 554,01 mg HAN â 63,21 % HAN
2   V/ML   13.279   PH   9.941   â 1,742 ml â 184,83 mg (TEAN+NH₄NO₃)
                                  â 21,09 % (TEAN+NH₄NO₃)

BUR. V/ML   20.0   REAGENT 0,5 n KOH wäßr. Titrisol
TEMP/C   22.0   TITER 1,000
KIMET D   4.0   ELECTRODES kombinierte Glaselektrode Metrohm
MPD VAR   4.0   SAMPLE 876,4 mg LP 1845
START V/ML   0.000
STOP PH   100.000
STOP V/ML   20.000   REMARKS 40 ml H₂O + 10 ml Aceton
STOP # EP   9.0   DATE 12.9.86   NAME Ja
047

Fig. 12.1: Analysis of LP 1845: Simultaneous determination of HAN
           and TEAN by substitution titration: 1st derivative.
           Here: 1) Determination of HAN after acetoxim formation
                    by the addition of acetone
                 2) Determination of TEAN.

Fig. 13:   Steam distillation unit after Ströhlein.

Fig. 14: Diagrammatic representation of the steam distillation unit:
(1) Inlet connection for the sample, (2) Boiler inlet tube, (3) Electric boiler, (4) Drop separator, (5) Collector flask, (6) Spiral condenser, (7) Distilling flask, (8) Receiver.

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Fig. 15:   DSC spectra of dehydrated NOS-365 as depending on the
pH value. Weight of sample 15 mg; heating rate: 6 °C
(10.8 °F) per minute.

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Fig. 16: Storage time of LP 1846 as depending on metal ion concentration (V, Cu, Fe). Accelerated storage tests in pressure testing apparatus at 90 °C. Final pressure: 4 bar.

Fig. 17: Pressure/time curves of contaminated LP 1846. Metal ion concentration 10 ppm. Accelerated storage tests in pressure testing apparatus at 90 °C.

pressure in bar

storage duration in days

LP 1846 + 10ppm Fe^{2+}

LP 1846 + 10ppm Fe^{2+}
+ Deguest 2041

Original LP 1846

Fig. 18: Pressure/time curves of LP 1846: original;
contaminated (10 ppm Fe^{2+}); contaminated with 10 ppm
Fe^{2+} and stabilized with Dequest 2041 (Fe/Dequest =
1/10). Accelerated storage tests in pressure testing
apparatus at 90 °C (194 °F).

LP-Type		LP 1845	LP 1845	LP 1846
HAN-producer or LOT-No.		BASF	THIOKOL	LOT 49-1
HAN [Wt-%]		60,04	63,01	61,43
TEAN [Wt-%]		18,37	20,14	18,54
IPAN [Wt-%]		-	-	-
H_2O [Wt-%]		19,49	16,07	19,50
NH_4NO_3 [Wt-%]		2,10	0,47	0,53
HNO_3 [Wt-%]		0,00	0,31	0,00
HNO_3 [moles/l]		0,00	0,05	0,00
pH (diluted 1:1)		2,741	0,974	1,705
Density 25 °C [g/cm³]		1,462	1,466	1,445
AAS in ppm	Detection limit			
Cu	0,1	0,02	0,02	0,02
Zn	0,2	-	-	-
V	1,7	<1,9	<2,0	<2,0
Cr	0,2	0,33	0,02	0,13
Mo	0,6	<2,0	<2,0	<2,0
W	11,0	<11	<11	<11
Mn	0,05	0,00	0,01	0,03
Fe	0,1	0,90	0,10	0,10
Co	-	-	-	-
Ni	0,1	0,37	0,37	0,26
Sn	1,0	-	-	-
Na	0,1	-	-	-
Ca	-	-	-	-

Table 1: Analysis values for monergols containing HAN.

Material	17/4 PH	V 2A	V 4A	30 Cr Ni Mo 8V	35 Ni Cr Mo V 125
Material No.	1.4542	1.4541	1.4571	1.6580	1.2760
C	< 0,07	≤ 0,06	0,06	0,26-0,33	0,35
Si	< 1	≤ 1	≤ 1	0,25	0,2
Mn	< 1,00	≤ 2	≤2	0,45	0,5
P	< 0,04			0,035	
S	< 0,03				
Cr	15,5-17,5	17-19	16,5-18,5	2,0	1,4
Mo	-		2-2,5	0,4	0,3
Ni	3,00-5,00	9-11,5	10,5-13,5	2,0	4,0
Cu	3,00-5,00				
Nb + Ta	0,15-0,45				
Ti		0,3	0,3		

Table 2: The composition of stainless steels.

Metal	Decomposition time in days	Relative decomposition time in %	Remarks
– (Original LP)	68.6	100.0	colourless
Lead	70.3	102.5	"
Silver	70.1	102.2	"
Tantalum	69.9	101.8	"
Gold	69.5	101.5	"
Zinc	69.2	100.9	dissolved
Mercury	68.2	99.0	colourless
Manganese	67.8	98.8	dissolved
Aluminium	63.4	92.4	colourless
Iridium	62.0	90.4	"
Silicon	57.0	83.1	"
Nickel	56.8	82.8	green
Cobalt	55.6	81.0	pink
Platinum	56.7	82.7	colourless
Molybdenum	47.8	69.7	dissolved
Tin	45.0	65.6	dissolved
Titanium	42.0	61.2	colourless
Tungsten	34.4	49.7	"
Chromium	23.4	34.1	"
Antimony	4.0	5.8	"
Copper	1.6	2.3	green
Rhenium	1.ʳ	2.2	colourless
Iron	...	1.5	yellowish-green
Vanadium			
Zirkonium			
Alloys			
V 4A (1.4571)	50.4	73.5	colourless
17/4 PH (pressure transducer) (1.4542)	15.7	22.9	"
V 2A (1.4541)	1.8	2.6	"
30 Cr Ni Mo 8 V (1.6582)	0.8	1.1	"
35 Ni Cr Mo V 125 (1.2760)	0.5	0.7	colourless

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

Chemical name	Abbreviation	Colour	Supplier
Ethylene-Propylene-Diene Copolymers	EDPM	black	Freudenberg, D-6940 Weinheim, FRG
Vinylidenefluoride-Hexafluor-propylene Copolymers (Viton)	FPM	black-brown	Ulman, D-7032 Sindelfingen 6, Otto-Hahnstr. 17, FRG
Acrylnitrile-Butadiene Copolymers	NBR	black	Freudenberg (as above)
Silicone Resin	VMQ	red	Ulman (as above)
Ethylene-Propylene Copolymers	EP	black	Ulman (as above)
Polytetrafluoroethylene	PTFE (PT 950)	white	Gehrckens, D-2080 Pinneberg, FRG
Polytetrafluoroethylene	PTFE (TFM)	white	Beichler & Grünewald, 7121 Lochgau, FRG
Tetrafluoroethylene-Perfluoro-alkylvinyl Ether Copolymers	PFA, TFA	opales-cent white	Beichler & Grünewald
Polytrifluorochloroethylene	PCTFE	transpa-rent-turbid	Beichler & Brünewald
Perfluorelastomer	Kalrez 4079	black	Du Pont, D-4000 Düsseldorf, FRG

Table 4: The selection of suitable sealing materials.

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	"
Kalrez 4079	36.8	"	42.5	"

Table 5: The influence of sealing materials on the chemical stability of LP 1846. Accelerated storage test in glass ampoules at 90 °C (194 °F).

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 6: The permeation coefficients P of sintered PTFE (Hostaflon, manufactured by Hoechst AG, FR Germany) at room temperature in accordance with German Standard DIN 53380. Units of P as in Table 7

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 7: The temperature dependency of the permeation coefficients P of PTFE (Hostaflon) with Helium.

Temperature	Gas					
in °C	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 8: The temperature dependency of the permeation
coefficients P of amorphous PCTFE (Voltalef 300)
for a number of gases. Permeation coefficient x 10^{10}.

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Gas	PTFE (Hostaflon)				PCTFE	
	TF 1740		TFM 1700		Voltalef 300	
	25 °C	90 °C	25 °C	90 °C	25 °C	90 °C
N_2	$1.25 \cdot 10^{-2}$		$9.5 \cdot 10^{-3}$		$5.1 \cdot 10^{-5}$	$2.0 \cdot 10^{-3}$
O_2	$3.92 \cdot 10^{-2}$		$2.52 \cdot 10^{-2}$		$4.1 \cdot 10^{-4}$	$1.1 \cdot 10^{-2}$
CO_2	$1.1 \cdot 10^{-1}$		$7.1 \cdot 10^{-2}$		$1.4 \cdot 10^{-3}$	$2.7 \cdot 10^{-2}$
He	$3.83 \cdot 10^{-1}$	1.26				

Table 9: Gas fluxes Q ((in cm^3/day) through PTFE and PCTFE sealing materials at Δp = 5 bar and at 25 and 90 °C (77 and 194 °F), calculated for flat sealing elements (r_0 = 6 mm; r_i = 4 mm; d = 2 mm; A = 0.63 cm^2) of the testing apparatus.

| t | Tc | P | t | Tc | P |
Tage	°C	bar	Tage	°C	bar
0	22.0	2.05	17	20.5	1.97
1	21.0	2.01	18	20.2	1.98
2	20.0	2.00	19	20.0	1.99
3	20.0	2.01	20	20.7	2.00
4	20.0	2.00	24	19.9	1.95
7	21.5	2.05	25	19.8	1.95
8	21.5	2.08	29	21.0	1.98
9	21.3	2.06	30	22.8	2.02
10	20.5	2.03	31	23.0	2.04
11	19.0	2.01	32	22.8	2.07
13	19.5	2.00	33	19.3	2.04
14	20.4	2.00	35	19.0	2.02
15	19.3	1.98	36	19.9	2.03
16	18.9	1.96			

Table 10: Gas pressure p (in bar) in glass containers at 25 °C
(77 °F) as depending on time t (in days); T_c =
measurement temperature in °C.

No.	Propellant Components	K_A $\dfrac{mol^2}{dm^{-6}}$	pK_A	pK_B	pK_B (literature values)	Literature quote
1	1	2	3	4	5	6
1	Hydroxylammonium nitrate (HAN) + formaldehyde (formaldoxim)	$0.245 \cdot 10^{-1}$	1.61	12.56	./.	./.
2	Hydroxylammonium nitrate (HAN) + acetone (acetoxim)	$0.191 \cdot 10^{-1}$	1.72	12.45	12.19	|18|
3	Ammonium nitrate (AN) + formaldehyde (hexamethylene tetramine)	$0.141 \cdot 10^{-5}$	5.85	8.32	8.85 9.1	|19| |17|
4	Hydroxylammonium nitrate (HAN)	$0.733 \cdot 10^{-6}$	6.135	8.035	8.03	|18|
5	Triethanol ammonium nitrate (TEAN)	$0.112 \cdot 10^{-7}$	7.95	6.22	6.23	|18|
6	Ammonium nitrate (AN)	$0.331 \cdot 10^{-9}$	9.48	4.69	4.75	|18|
7	Isopropyl ammonium nitrate (IPAN)	$0,138 \cdot 10^{-10}$	10.86	3.31	3.37	|18|

Table 11: Dissociation constants K_A as well as relevant pK_A and pK_B values of several propellant components in aqueous solution at 20 °C.

Propellant	No.	Component	$\overline{x}$ in wt.%	s in wt.%	V in rel.%	n
		1	2	3	4	5
LP 1845	1	HAN	62,90	0,12	0,18	12
	2	TEAN	19,77	0,38	1,91	12
	3	AN	0,47	0,06	13,7	2(!)
	4	HNO$_3$	0,31	0,0082	2,63	4
LP 1846	5	HAN (alkalim.)	61,37	0,074	0,121	11
	6	HAN (oxidim.)	60,90	0,027	0,04	3
	7	TEAN	18,60	0,2	1,07	3
	8	AN	0,53	--	--	3
	9	HNO$_3$	0	--	--	-

Table 12: Characteristics $\overline{x}$, s, V and n for the statistical evaluation of propellant analyses.

Metal ions	Relative decomposition time in %			
	2	5	10	100
W^{6+}	115	120	103	104
Zr^{4+}	104	98	100	102
Cr^{3+}	–	–	(92)	100
Mn^{2+}	106	102	101	97
Mg^{2+}	–	98	95	96
Pb^{2+}	94	88	87	96
Sn^{2+}	103	98	100	92
Ag^{+}	101	99	93	92
Ce^{+}	103	98	(80)	91
Zn^{2+}	99	100	(84)	90
Ni^{2+}	105	97	99	89
Al^{3+}	101	88	(80)	87
Cd^{2+}	96	94	(80)	86
B^{3+}	102	97	96	85
Co^{2}	100	99	97	80
Hg^{2+}	98	100	102	79
Mo^{6+}	–	–	98	69
Ti^{4+}	109	95	98	(66)
Bi^{3+}	93	100	93	54
Pd^{2+}	101	94	8	52
Cu^{2+}	73	59	48	17
V^{4+}	71	59	40	13
Fe^{3+}	55	36	24	4
Fe^{2+}	57	31	20	4

Table 13: Comparison of the relative decomposition times of LP 1846. Accelerated storage tests in glass ampoules at 90 °C (194 °F). Metal ion concentrations of 2, 5, 10 and 100 ppm.

Metal ions	Relative decomposition time in %					
	0,5	1	2	5	10	100
Pd^{2+}	98	100	101	94	78	52
Cu^{2+}	84	87	73	59	48	17
V^{4+}	89	88	71	59	40	13
Fe^{2+}	77	71	57	31	20	4

Table 14: Comparison of the relative decomposition times of LP 1846. Accelerated storage tests in glass ampoules at 90 °C (194 °F). Metal ion concentration from 0.5 to 100 ppm.

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

Table 15: 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 (194 °F).
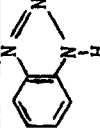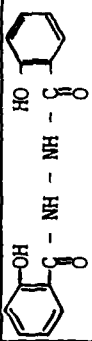
Trade Name	Structural Formula	Chemical Name	Supplier
Turpinal SL	HO−P−C−P−OH (with CH₃, OH, OH, O groups)	1-Hydroxy-ethylidene-1,1-disphosphonic acid	Henkel KG Postfach 11 00 D-2000 Düsseldorf
Turpinal D 2	N[−CH₂−P(=O)(OH)−OH]₃	Amino-tris-(methylene phosphonic acid)	Henkel KG
Remomet BTA-M	(benzotriazole structure)	Benzotriazole	Ciba-Geigy CH-4002 Basel
GI 09-215/3	(N,N'-disalicyloyl-hydrazine structure)	N,N'-Disalicyloyl-hydrazine	Ciba-Geigy
Dequest 2000	identical with Turpinal SL	see above	Brenntag AG Postfach 10 03 52 4330 Mülheim-Ruhr 1
Dequest 2010	identical with Turpinal D 2	see above	Brenntag AG
Dequest 2041	(HO−P(=O)(OH)−CH₂)₂N(CH₂)₂N(−CH₂−P(=O)(OH)−OH)₂	Ethylenediamine-tetra-(methylene phosphonic acid)	Monsanto Europe N.V. Scheldelaan B-2040 Antwerpen
Dequest 2060 S	HO−P(=O)(OH)−CH₂−N[−CH₂CH₂−N(−CH₂−P(=O)(OH)−OH)₂]₂	Diethylenetriamine-penta-(methylene phosphonic acid)	Monsanto Europe N.V.
Dequest 2056	(HO−P(=O)(OH)−CH₂)₂N(CH₂)₆N(−CH₂−P(=O)(OH)−OH)₂	Hexamethylenediamine-tetra-(methylene phosphonic acid)	Monsanto Europe N.V.

Table 16: Selection of complexing agents.

stabilizer	iron : stabilizer 1 : 1 in moles	iron stabilizer 1 : 10 in moles
- without stabilizer	17.4	17.4
Turpinal SL	19.8	25.0
Turpinal D2	34.2	42.5
Dequest 2041	29.2	47.4
Dequest 2060 S	18.3	11.8
Dequest 2060 S (free from HCL)	-	39.0
Dequest 2056	-	19,5
Dequest 2056 (free from HCL)	-	-
Benzotriazole	-	18.4
N,N'-Disalicyloyl-hydrazine	-	19.2
1-Nitroso-2-naphthol	-	26.7
1,2-Cyclohexanedione	-	19.7
α-Dimethylglyoxime	-	20.6
Tris [2-(2-methoxy-ethoxy)-ethyl]amine	-	20.8
Quinaldine acid	-	18.2
Thioglycolic acid	-	19.2
Dithiooxamide	-	18.9
Titriplex II (EDTA)	-	21.0
Titriplex IV (CDTA)	-	25.1
Urea	-	19.1
Zincon	-	17.3
Tributylphosphate	-	22.5
2,4,6-Tri-(2-pyridyl-s-triazine)	-	19.3
Nitroso-R-salt	-	19.1
α, α' - Dipyridyl	-	19.2

Table 17: The influence of stabilizers on the spontaneous decomposition of LP 1846 contaminated with 10 ppm iron ions. Decomposition times in days. Accelerated storage tests in glass ampoules at 90 °C (194 °F).

Stabilizer	Decomposition time in days	
	Cu^{2+} (100 ppm)	Fe^{2+} (100 ppm)
- (without stabilizer)	15.⸳	3.5
Turpinal SL	17.2	4.2
Turpinal D2	1S.3	6.0
Dequest 2041	15.4	13.5
Dequest 2060 S	4.0	5.0
Dequest 2060 S (free from HCL)	17.1	5.0
Dequest 2056	1.5	7.5
Dequest 2056 (free from HCL)	16.3	-
Benzotriazole	14.5	3.0
N,N'-Disalicyloyl-hydrazine	15.1	3.0
1-Nitroso-2-naphthol	15.2	3.0
1,2-Cyclohexanedione	17.9	3.0
α-Dimethylglyoxime	19.8	3.0
Tris[2-(2-methoxy-ethoxy)-ethyl]amine	16.8	4.5
Quinaldine acid	20.3	4.5
Thioglycolic acid	18.9	4.5
Dithiooxamide	17.8	4.0
Titriplex II (EDTA)	16.3	4.5
Titriplex IV (CDTA)	16.9	5.2
Urea	18.0	3.5
Zincon	11.6	2.9
Tributylphosphate	2.0	5.5
2,4,6-Tri-(2-pyridyl-s-triazine)	19.7	4.5
Nitroso-R-salt	15.3	4.0

Table 18: The influence of stabilizers on the spontaneous decomposition of LP 1846 contaminated with 100 ppm copper and iron ions. Decomposition times in days. The molar ratio between metal ions and stabilizer is 1 : 1. Accelerated storage tests in glass ampoules at 90 °C (194 °F).

Ion concentration in ppm		Decomposition time in days
iron	copper	
0	0	90,8
1	1	55,7
1	2	54,3
2	0	51,9
0	2	66,2
2	1	50,2
2	2	44,6
3	7	33,1
7	3	26,9
5	0	27,9
0	5	53,7
5	5	28,3
10	0	17,4
0	10	41,6
10	10	19,2
20	0	13,7
0	20	38,0

Table 19: The simultaneous influence of iron and copper ions on the spontaneous decomposition of LP 1846. Accelerated storage tests in glass ampoules at 90 °C (194 °F).

Metal ions (10 ppm)	storage time up to 4 bar (in days)	pH 1 : 1 dil.	NH₄NO₃ in %	HNO₃ in %	HAN in %	TEAN in %
Without metallic ions	42,5	0,57	1,79	1,36	57,37	17,02
Fe²⁺	8,2	0,22	2,41	2,07	55,23	18,76
Cu²⁺	12,0	0,39	3,29	2,11	54,08	20,45
V⁴⁺	7,3	0,42	1,71	1,60	56,58	18,60

Table 20: Analytical results of LP 1846 contaminated with metal ions after storage at 90 °C (194 °F) in a pressure testing apparatus.

iron concentration in ppm	storage time in days	pH 1 : 1 dil.	NH_4NO_3 in %	HNO_3 in %	HAN in %	TEAN in %
0	42,5	0,57	1,79	1,36	57,37	17,02
1	31,2	0,56	2,10	1,61	56,33	17,33
2	22,6	0,28	2,03	1,49	56,55	18,09
3	18,9	0,26	1,94	1,52	56,81	18,35
5	13,6	0,32	1,90	1,83	56,39	17,84
10	8,2	0,22	2,41	2,07	55,23	18,76

Table 21: The influence of iron ions (between 0 and 10 ppm) on the storage time of LP 1846. The propellant composition after accelerated storage tests in pressure containers at 90 °C (194 °F). The final pressure was 4 bar.

copper concentration in ppm	storage time in days	pH 1 : 1 dil.	NH₄NO₃ in %	HNO₃ in %	HAN in %	TEAN in %
0	42,5	0,57	1,79	1,36	57,37	17,02
1	37,4	0,50	1,96	1,46	56,95	17,71
2	32,9	0,52	1,60	1,39	56,93	18,79
3	31,1	0,44	1,81	1,56	56,37	19,09
5	21,1	0,46	2,65	2,02	55,2	20,32
10	12,0	0,39	3,29	2,11	54,08	20,45

Table 22: The influence of copper ions (between 0 and 10 ppm) on the storage time of LP 1846. The propellant composition after accelerated storage tests in pressure containers at 90 °C (194 °F). The final pressure was 4 bar.

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vanadium concentration in ppm	storage time in days	pH 1 : 1 dil.	NH₄NO₃ in %	HNO₃ in %	HAN in %	TEAN in %
0	42,5	0,57	1,79	1,36	57,37	17,02
1	27,6	0,50	1,51	1,39	56,63	18,67
2	18,8	0,53	1,56	1,49	56,83	18,69
3	15,6	0,50	1,56	1,52	56,78	18,70
5	10,4	0,47	1,66	1,58	56,52	18,74
10	7,3	0,42	1,71	1,60	56,58	18,60

Table 23: The influence of vanadium ions (between 0 and 10 ppm) on the storage time of LP 1846. The propellant composition after accelerated storage tests in pressure containers at 90 °C (194 °F). The final pressure was 4 bar.

Addition	storage time up to 4 bar (in days)	pH 1:1 dil.	NH_4NO_3 in %	HNO_3 in %	HAN in %	TEAN in %
Without	42.5	0.57	1.79	1.36	57.37	17.02
Fe^{2+} (10 ppm)	8.2	0.22	2.41	2.07	55.23	18.76
Fe^{2+} (10 ppm) + Dequest 2041 Molar ratio 1:10)	31.5	0.53	1.61	1.64	56.35	19.66

Table 24: Analytical results of LP 1846 contaminated with metal ions after storage at 90 °C (194 °F) in a pressure-testing apparatus. The final pressure was 4 bar.