

**Federal Institute for Materials Research and Testing
Laboratory II.22
Safety Related Properties of Gases**

To Diary-No. II.2-360/95

Berlin, May 23, 1995

Chemical stability of ethylene oxide and 1,2-propylene oxide in the presence of the sealing material "SIGRAFLEX-HOCHDRUCK"

At the request from February 19, 1992 of the firm Sigrü GmbH ethylene oxide and 1,2-propylene oxide were investigated for their chemical stability in contact with a sealing material at the Federal Institute for Material Research and Testing (BAM). According to the specification by the applicant the material is an impregnated composite material without bonding agent consisting for instance of 4 graphite foil layers (0.5 mm) and 3 layers stainless steel sheet (0.05 mm).

It was confirmed that ethylene oxide and 1,2-propylene oxide remain stable in the presence of the sealing material by warm storage tests for 6 weeks with ethylene oxide at 40 °C, and with 1,2-propylene oxide at 60 °C. Under the given experimental conditions no change owing to the influence of the sealing material on ethylene oxide and 1,2-propylene oxide could be detected. The ignition temperatures did not change. The sealing material was not dissolved by either of the alkene oxides. The slightly enlarged amount of evaporation residue in the case of ethylene oxide stored in contact with the sealing material was identified as polyethylene oxide to 89 %, thereby it was also found that the residue does not consist of soluble parts of the sealing material [1].

The retail name of the sealing material has been SIGRAFLEX-HOCHDRUCK V(050-400)10C3I. Another sealing material called SIGRAFLEX-HOCHDRUCK V(050-400)11Z3I is nearly identical with the sealing material investigated at the BAM [2].

On the part of the BAM there are no objections to change the retail name to SIGRAFLEX-HOCHDRUCK provided that the composition of the sealing material is identical with that of the sealing material SIGRAFLEX-HOCHDRUCK V(050-400)10C3I, investigated at the BAM, or with that of the sealing material SIGRAFLEX-HOCHDRUCK V(050-400)11Z3I respectively [1][2].

On the part of the BAM there are no objections against the use of the report, and its supplement, about the investigation of the chemical stability of ethylene oxide and 1,2-propylene oxide in the presence of the sealing material SIGRAFLEX-HOCHDRUCK V(050-400)10C3I and SIGRAFLEX-HOCHDRUCK V(050-400)11Z3I - now called SIGRAFLEX-HOCHDRUCK - by SGL-TECHNIK GmbH [1][2].

by order

Ulrich Seidelmann



Ulrich Seidelmann

- [1] Report of the Federal Institute for Materials Research and Testing, Laboratory 4.21 to Diary-No. 4.2-159/92 from June, 4, 1992 about the investigation of the chemical stability of ethylene oxide and 1,2-propylene oxide in the presence of the sealing material "SIGRAFLEX-HIGH PRESSURE V(050-400)10C3I"
- [2] Supplement to Report of the Federal Institute for Materials Research and Testing, Laboratory 4.21 to Diary-No. 4.2-159/92 from June 4, 1992 about the investigation of the chemical stability of ethylene oxide and 1,2-propylene oxide in the presence of the sealing material "SIGRAFLEX-HIGH PRESSURE V(050-400)10C3I"

BAM Diary-No. 4.2-458/93 from April, 24, 1993

-Federal Institute for Materials Research and Testing-
BUNDESANSTALT FÜR MATERIALFORSCHUNG UND -PRÜFUNG
(BAM)

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To Diary-No. 4.2-159/92

Berlin, June, 4, 1992

R e p o r t

about the investigation of the chemical stability of ethylene oxide and 1,2-propylene oxide in the presence of the sealing material "SIGRAFLEX-High Pressure V(050-400) 10 C3I"

1. Application

The Firm SIGRI GmbH, Meitingen has applied for investigations of the chemical stability of ethylene oxide and 1,2-propylene oxide in contact with the sealing material "SIGRAFLEX-High Pressure V(050-400) 10 C3I" at the Federal Institute for Materials Research and Testing (BAM) with the letter HLE/Mec from February 19, 1992. By means of these investigations it shall be determined, whether the sealing material conforms with the "Rules for the construction of ships for the Transport of liquefied gases as bulk cargo" by the German Lloyd.

2. Investigation material

2.1 Sealing material

Rectangular blanks of dimensions 120 mm x 20 mm x 2 mm and rings of outside diameter 190 mm, inside diameter 140 mm and a thickness of 2 mm consisting of the material with the name "SIGRAFLEX-High Pressure V(050-400) 10 C3I", in following called "V(050-400) 10 C3I", were made available as investigation material to the BAM. According to the firm SIGRI GmbH the material is an impregnated composite material without bonding agent consisting of 4 graphite foil layers (0,5 mm) and 3 layers of stainless steel sheet (0,05 mm). The numbers in parentheses in the name of the material give the thicknes of the material in 1/100 mm, e.g. V(050-400) 10 C3I = 0,50-4,00 mm.

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2.2 Ethylene oxide; 1,2-Propylene oxide

The ethylene oxide was obtained from the firm Linde AG with the following specification.

percentage purity: 2.7 = 99.7%
manufacturing date: 45. calendar week 1991
(start of investigation
12. calendar week 1992)
evaporation residue: 0.02 %

The 1,2-propylene oxide was obtained from the firm E. Merck Darmstadt with the following specification.

quality: 1,2-propylene oxide for synthesis
content: more than 99%
evaporation residue: 0.004 %

3. Investigation programme

3.1 Warm storage tests

One litre of ethylene oxide and one litre of 1,2-propylene oxide, respectively, were stored in contact with 5 blanks "V(050-400) 10 C3I" each in special autoclaves of stainless steel in warming cupboards. Before that the blanks were exposed to a temperature of 60°C in a drying chamber, cooled to room temperature in an exsiccator above silica gel (blue gel) and weighed on an analytical balance. The autoclaves were sealed with rings of "V(050-400) 10 C3I". The storage temperature was 40°C for the test with ethylene oxide and 60°C for the test with 1,2-propylene oxide. The duration of the storage was 6 weeks.

The analogous storage tests were carried out without the addition of "V(050-400) 10 C3I". In these tests the autoclaves were sealed with rings of PTFE.

The pressure within the autoclaves and the temperature of the autoclaves were continuously measured during the storage time and automatically recorded. The temperature in the warming cupboards was also measured and recorded for the, if necessary, unequivocal determination of temperature and pressure changes due to chemical reactions and not to the change of environmental temperature.

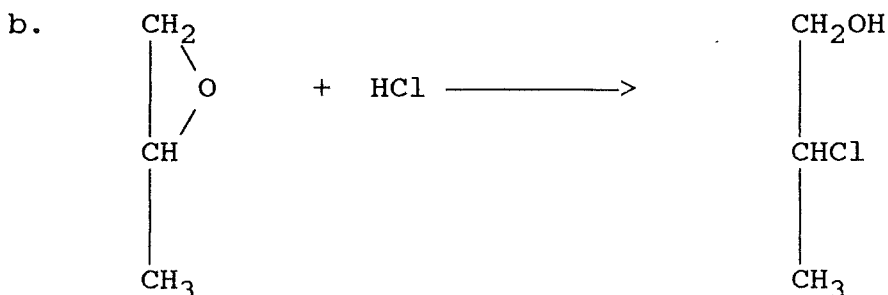
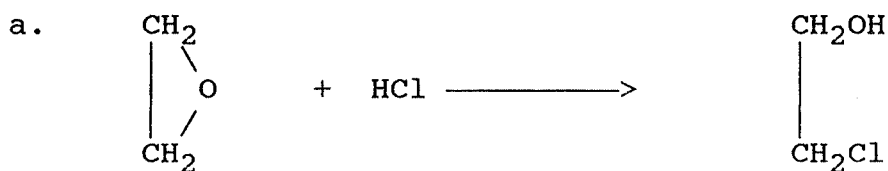
During the six weeks-storage no pressure and temperature changes caused by any reaction were observed.

3.2 Analytical investigations

3.2.1 Determination of the contents of ethylene oxide and 1,2-propylene oxide according to a method by Deckert[1] [2] and Kerkow[3].

Principle:

Ethylene oxide and 1,2-Propylene oxide, respectively, react with hydrochloric acid saturated with metal chlorides to 2-chloroethanol and to 2-chloropropanol, respectively.



[1] Deckert W.	Fr. Z. f. Anal. Ch.	82	297	(1930)
[2] Deckert w.	Ang. Chem.	45	785	(1932)
[3] Kerkow F.W.	Fr. Z. f. Anal. Ch.	108	249	(1937)

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The consumption of hydrochloric acid is the measure for the content of ethylene oxide and 1,2-propylene oxide, respectively.

There were determined

- a) non-stored
- b) stored for 6 weeks at 40°C and 60°C, resp.
- c) stored for 6 weeks at 40°C and 60°C, resp.,
in contact with "V(050-400) 10 C3I"

samples of ethylene oxide and 1,2-propylene oxide, resp., each time.

The results for the samples stored with and without "V(050-400) 10 C3I" agree with the results for the unstored samples within the limits of the relative errors of the analytical method. A change caused by the influence of "V(050-400) 10 C3I" on ethylene oxide and 1,2-propylene oxide, resp., was not established.

3.2.2 Gravimetric determination of the "V(050-400) 10 C3I" blanks charged by ethylene oxide and 1,2-propylene oxide, respectively

The "V(050-400) 10 C3I" blanks stored together with ethylene oxide and 1,2-propylene oxide, resp., were treated and weighed as described in section 3.1 after removal of the ethylene oxide and propylene oxide fractions, resp., by evaporation.

A loss in weight was not established, "V(050-400) 10 C3I" is not dissolved by either of the alkene oxides.

3.2.3 Determination of the evaporation residues

Samples of ethylene oxide and 1,2-propylene oxide - unstored, warmly stored for 6 weeks, and warmly stored for 6 weeks in contact with "V(050-400) 10 C3I" - were evaporated and the masses of the residues were determined.

Results

Ethylene oxide	unstored	0,02 % residue
Ethylene oxide	stored at 40°C without "V(050-400) 10 C3I"	0,14 % residue
Ethylene oxide	stored at 40°C with "V(050-400) 10 C3I"	0,15 % residue
1,2-Propylen oxide	unstored	0,004 % residue
1,2-Propylen oxide	stored at 60°C without "V(050-400) 10 C3I"	0,031 % residue
1,2-Propylen oxide	stored at 60°C with "V(050-400) 10 C3I"	0,039 % residue

Under the given experimental conditions there were found only slightly higher amounts of residues in the samples of ethylene oxide and 1,2-propylene oxide, resp., stored in contact with "V(050-400) 10 C3I" than in the samples of ethylene oxide and 1,2-propylene oxide, resp., stored without that addition.

3.2.4. Investigation of the evaporation residue for the content of polyalkene oxide

The evaporation residue of the ethylene oxide sample stored in contact with "V(050-400) 10 C3I" was investigated according to the method published by Seher [4] which principle is described in the following.

After oxonation of the polymerizate with barium chloride in acid medium and precipitation of the formed oxonium kation with sodium tetraphenylborate solution the complex precipitate is sucked off. After being dissolved in dimethylformiate the complex is decomposed by merkury(II) nitrate, the excess of mercury(II) nitrate is back-titrated according to the method of Vollhard. The consumption of mercury(II) nitrate is the measure for content of polyalkene oxide.

A mass fraction of 89 % was found for polyalkene oxide. Thereby it was established that the evaporation residue of the ethylene oxide stored in contact with "V(050-400) 10 C3I" does not consist of soluble parts of sealing material.

The amount of the evaporation residue of the 1,2-propylene oxide stored in contact with "V(050-400) 10 C3I" is too small to carry out a quantitative determination of polyalkene oxide parts.

3.2.5 Determination of the ignition temperatures

The ignition temperatures according to the german standard DIN 51 794 were determined for ethylene oxide and 1,2-propylene oxide warmly stored with and without contact with "V(050-400) 10 C3I".

No differences were found. The ignition temperatures of ethylene oxide and 1,2-propylene oxide were not reduced by the warm storage in contact with "V(050-400) 10 C3I".

4. Summary and review

On application of the firm SIGRI GmbH, Meitingen, ethylene oxide and 1,2-propylene oxide were investigated for their chemical stability in contact with the sealing material "SIGRAFLEX-High Pressure V(050-400) 10 C3I" described in section 2.1. It was confirmed that ethylene oxide and 1,2-propylene oxide remain stable in the presence of the sealing material "SIGRAFLEX-High Pressure V(050-400) 10 C3I" by warm storage tests for 6 weeks with ethylene oxide at 40°C, and with 1,2-propylene oxide at 60°C. Under the given experimental conditions no change owing to the influence of the sealing material "SIGRAFLEX-High Pressure V(050-400) 10 C3I" on ethylene oxide and 1,2-propylene oxide could be detected. The ignition temperatures did not change. The sealing material "SIGRAFLEX-High Pressure V(050-400) 10 C3I" was not dissolved by either of alkene oxides. The slightly enlarged amount

of evaporation residue in the case of ethylene oxide stored in contact with the sealing material "SIGRAFLEX-High Pressure V(050-400) 10 C3I" was identified as polyethylene oxide to 89 %, thereby it was also found that the residue does not consist of soluble parts of the sealing material "SIGRAFLEX-High Pressure V(050-400) 10 C3I".

On the part of the BAM there are no objections to using the material "SIGRAFLEX-High Pressure V(050-400) 10 C3I" as sealing material in contact with ethylene oxide and 1,2-propylene oxide each with the specification described in section 2.2, if the special requirements of the German Lloyd [5] for ethylene oxide 17.16 and for 1,2-propylene oxide 17.20 are observed, particularly the temperature of 30°C for the transport of ethylene oxide given under 17.16.6.

by order

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[5] German Lloyd; Prescriptions for the classification and construction of steel sea-boats, edition 1987, chapter 9, prescriptions for ships for the transport of liquefied gases as bulk cargo.