BAM
Bundesanstalt für
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und -prüfung

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TEST REPORT

on Testing a Nonmetallic Material for Reactivity with Oxygen

Reference Number	17014485 III E
Our Reference	02-3383
Copy	1. copy of 2 copies
Customer	Klinger AG Egliswil Webereistraße 1 5704 Egliswil Switzerland
Date of Request	February 20, 2017
Your Reference	- - -
Receipt of Signed Contract	August 24, 2017
Test Samples	Graphite-based material KLINGER Graphit-Laminat SLS-MULTI PLUS, undisclosed batch;
Receipt of Samples	October 4, 2017 and January 2, 2018
Test Date	October 12, 2017 to January 12, 2018
Test Location	BAM – Division 2.1 „Gases, Gas Plants"; building no. 41
Test Procedure or Requirement according to (in the current version)	DIN EN 1797 und ISO 21010 "Cryogenic Vessels - Gas/Material Compatibility"; Annex of code of practice M 034-1 (BGI 617-1) "List of nonmetallic materials compatible with oxygen", by German Social Accident Insurance Institution for the raw materials and chemical industry; TRGS 407 Technical Rules for Hazardous Substances "Tätigkeiten mit Gasen - Gefährdungsbeurteilung" chapter 3 "Informationsermittlung und Gefährdungsbeurteilung" and chapter 4 "Schutzmaßnahmen bei Tätigkeiten mit Gasen"

All pressures of this report are excess pressures.
This test report consists of page 1 to 11 and annex 1 to 5.

2015-06 / 2015-09-17

2015-06

TEST REPORT

1 Documents and Test Samples

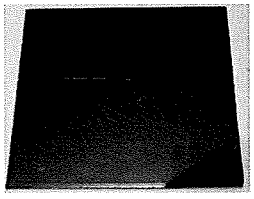
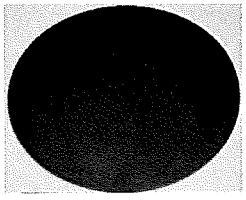
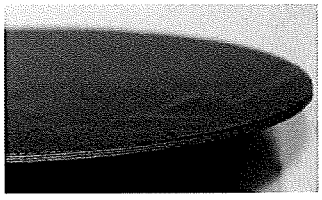
The following documents and samples were submitted to BAM:

1 Test application
Safety-related investigation on KLINGER Graphit-Laminat SLS-MULTI PLUS, undisclosed batch, for use as a sealing material in gaseous oxygen service at temperatures up to 250 °C, for use as a gasket material in flanges for gaseous oxygen service at temperatures up to 250 °C and at pressures up to 160 bars as well as for use in liquid oxygen service

1 Certificate of Conformity
(1 page, Klinger AG Egliswil, date of issue: 12.07.2017)

5 Sheets KLINGER Graphit-Laminat SLS-MULTI PLUS
(delivered October 4, 2017)
Dimensions: 150 mm x 150 mm, thickness: 2 mm
Color: Grey

20 Disks KLINGER Graphit-Laminat SLS-MULTI PLUS
(delivered January 2, 2018)
Dimensions: Outer diameter: 140 mm, Thickness 2 mm
Color: Grey

2 Applied Test Methods

The product KLINGER Graphit-Laminat SLS-MULTI PLUS, undisclosed batch, shall be used as a sealing material in valves for gaseous oxygen service at temperatures up to 250 °C, as a gasket material in flanges for gaseous oxygen service at temperatures up to 250 °C and at pressures up to 160 bars as well as for liquid oxygen service.

The following test methods were applied:

2.1 Testing for Ignition Sensitivity to Gaseous Oxygen Impacts

Generally, this test method is required if rapid oxygen pressure changes, so-called gaseous oxygen impacts, on the material cannot be safely excluded in usage.

2.2 Determination of the Autogenous Ignition Temperature (AIT) in High Pressure Oxygen

Usually, this test method is required if the material is for service temperatures greater than 60 °C.

The AIT is a safety characteristic and indicates the temperature at which the material shows self-ignition in the presence of oxygen without an additional ignition source.

Therefore, it is relevant for the maximum use temperature of a valve seal that is generally set 100 °C below this AIT. For gasket materials in flange connections, the safety margin between AIT and maximum use temperature is only 50 °C because of the particular mounting situation.

2.3 Testing for Aging Resistance in High Pressure Oxygen

This test is necessary whenever a material is intended for service at higher temperatures than 60 °C. It simulates the use of a material in practice and helps analyze whether ignition temperature or properties of the material change due to the aging processes.

2.4 Testing of Gaskets for Flanges in High Pressure Oxygen

This test simulates the faulty installation of a gasket in a flange connection where the sealing material projects into the inner diameter of the pipe. This test investigates the fire behavior of the gasket material in a standard flange after artificial ignition. It shows whether the fire of the disk is transferred to the metal of the flange or if the flange connection becomes leaky.

2.5 Testing for Reactivity with Liquid Oxygen on Mechanical Impact

Generally, this test method is required if direct contact of the material with liquid oxygen and mechanical impacts cannot be safely excluded in usage.

3 Preparation of Samples

To test the nonconductive gasket material, the disks were prepared as shown in figure 1.

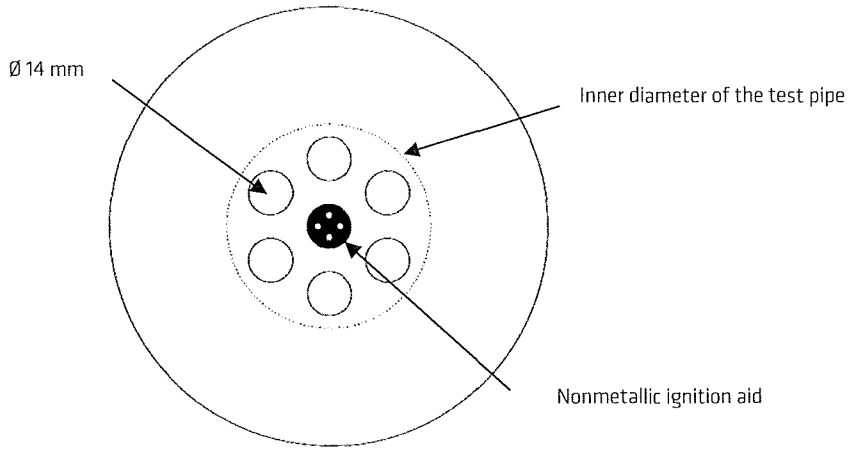


Figure 1: Preparation of the conductive flat gasket material

For all other tests, the disks were cut into parts of ca. 1 mm to 2 mm in edge length.

4 Tests

4.1 Testing for Ignition Sensitivity to Gaseous Oxygen Impacts

The test method is described in annex 1. Based on the specified use conditions by the customer, the test was performed at 60 °C and at 250 °C.

4.1.1 Assessment Criterion

According to DIN EN 1797 "Cryogenic Vessels - Gas/Material Compatibility" and to ISO 21010 "Cryogenic Vessels - Gas/Material Compatibility" the criterion for a reaction of the sample to gaseous oxygen impacts is a temperature rise of at least 20 °C.

If the sample exhibits a change of color, or of consistency after testing, this is also considered as a positive reaction by BAM for safety reasons, even if there is no temperature rise detectable of at least 20 °C.

4.1.2 Results

In each of the test series, the initial oxygen pressure p_I was at ambient pressure.

Sample Temperature t_I [°C]	Final Oxygen Pressure p_F [bar]	Reaction
60	300	no reaction*
60	350	no reaction*
60	400	no reaction*
60	450	no reaction*
60	450	no reaction*
250	450	no reaction*
250	450	no reaction*

* within a series of five consecutive impacts

In two separate test series, each consisting of a series of five consecutive impacts, no reaction of the material KLINGER Graphit-Laminat SLS-MULTI PLUS, undisclosed batch, with oxygen could be observed at following conditions:

Sample Temperature t_I [°C]	Final Oxygen Pressure p_F [bar]
60	450
250	450

The investigation was stopped at a final oxygen pressure of 450 bars, as this is the maximum operating pressure of the test facility.

4.2 Determination of the Autogenous Ignition Temperature (AIT) in High Pressure Oxygen

The test method is described in annex 2.

The AIT determination was performed at a final oxygen pressure of approximately 160 bars according to the intended use conditions mentioned by the customer.

4.2.1 Assessment Criterion

The criterion for a reaction of the sample with oxygen is a distinct increase in pressure and a more or less steep increase in temperature.

4.2.2 Results

Test No.	Initial Oxygen Pressure p_I [bar]	Final Oxygen Pressure p_F [bar]	AIT [°C]
1	61	161	> 500
2	61	163	> 500
3	61	163	> 500
4	61	161	> 500
5	61	161	> 500

In five separate tests, with a mean final oxygen pressure of 162 bars, no ignition of the sample could be detected up to temperatures of 500 °C. This temperature is also the maximum operating temperature of the test apparatus. Consequently, the AIT of the sample is higher than 500 °C.

4.3 Testing for Aging Resistance in High Pressure Oxygen

The test method is described in annex 3.

In general, artificial aging is carried out at the maximum use pressure and an elevated temperature, that is 25 °C above the maximum operating temperature. In this case, the test was carried out at a final oxygen pressure of 160 bars and at a temperature of 275 °C.

4.3.1 Assessment Criterions

There are three criteria for evaluating the aging behavior:

If there is a change in mass $\Delta m \leq 1$ %, the sample is aging resistant, in case of $\Delta m > 1$ % and $\Delta m \leq 2$ %, the sample is sufficient aging resistant, and in case of $\Delta m > 2$ %, the sample is insufficient aging resistant.

Changes in color, consistency, shape or surface texture of the sample or gas releases from the sample that can be detected after testing will be also considered by BAM.

The AIT of the aged sample is compared to the AIT of the non-aged sample. If there is a distinct deviation between both AITs, the lower value is considered for safety reasons.

4.3.2 Results

4.3.2.1 Testing for Change in Mass or Physical Appearance

Time [h]	Temperature [°C]	Oxygen Pressure [bar]	Mass Change [%]
100	275	160	- 1.4

After aging, the test sample was apparently unchanged but had lost 1.4 % in mass.

4.3.2.2 Determination of the AIT of the Aged Material in High Pressure Oxygen

The test method is described in annex 2.

The AIT test of the aged material was performed under the same conditions as described in chapter 4.2.

Test No.	Initial Oxygen Pressure p_I [bar]	Final Oxygen Pressure p_F [bar]	AIT [°C]
1	61	163	> 500
2	61	162	> 500
3	61	161	> 500
4	61	163	> 500
5	61	163	> 500

In five separate tests, with a mean final oxygen pressure of 162 bars, no ignition of the aged sample could be detected up to temperatures of 500 °C. This temperature is also the maximum operating temperature of the test apparatus. Consequently, the AIT of the aged sample is higher than 500 °C.

4.4 Testing of Gaskets for Flanges in High Pressure Oxygen

The test method is described in annex 4.

According to the use conditions given by the customer, the flange test was carried out at a final oxygen pressure of 160 bars and a temperature of 250 °C.

4.4.1 Assessment Criterion

If after artificial ignition only those parts of the gasket burn that project into the pipe and the fire is not transmitted to the flanges, and if the gasket does not burn between the flange faces and the flange connection is still gas tight, there are no objections regarding technical safety to use the gasket under the conditions tested. Such a positive result has to be confirmed in four additional tests.

If, however, the gasket burns between the flange faces or the flange connection becomes un-tight, the gasket material has not passed the test. In this case, the test may be continued at a lower temperature or oxygen pressure after consultation with the customer.

4.4.2 Results

Test Number	Temperature [°C]	Oxygen Pressure [bar]	Notes
1	250	160	All parts of the gasket burn that project into the pipe. The flange faces remain undamaged. The flange connection remains gas-tight.
2	250	160	Same behavior of test sample as in test no. 1
3	250	160	Same behavior of test sample as in test no. 1
4	250	160	Same behavior of test sample as in test no. 1
5	250	160	Same behavior of test sample as in test no. 1

In five tests at 250 °C and at a final oxygen pressure of 160 bars, only those parts of the disk burn that project into the pipe.

In all tests, the fire is neither transmitted to the steel nor does the sample burn between the flange faces. The flange remains gas-tight. After testing, the samples exhibit a thickness of 2 mm.

4.5 Testing for Reactivity with Liquid Oxygen on Mechanical Impact

The test method is described in annex 5.

4.5.1 Assessment Criterion

According to the BAM-Standard "Testing for Reactivity with Liquid Oxygen on Mechanical Impact", a nonmetallic material is not suitable for liquid oxygen service, if reactions occur with liquid oxygen at a drop height of 0.17 m (impact energy 125 Nm) or less.

4.5.2 Results

Test Series No.	Drop Height [m]	Impact Energy [Nm]	Behavior on Mechanical Impact
1	0.83	625	No reaction in 1 single test
2	1.00	750	No reaction in a series of 10 single tests

At a drop height of 1.00 m (impact energy 750 Nm) no reactions of the sample with liquid oxygen could be detected in a series of 10 single tests.

5 Summary of the Test Results

In two separate tests, each consisting of a series of five consecutive impacts, no reactions of the sample with oxygen could be observed at a final pressure of 450 bars at 60 °C and at 250 °C.

At a final oxygen pressure p_F of 160 bars, the test sample has an autogenous ignition temperature that is greater than 500 °C.

The material proved to be sufficient aging resistant at 275 °C and 160 bars oxygen pressure.

The investigation of the burning behavior of disks of the gasket material in a standard flange showed that at 250 °C and an oxygen pressure of 160 bars only those parts of the sample burn that project into the pipe. The sample does not burn between the flange faces. In all cases the flange connection remained gas-tight.

Testing of the material for reactivity to mechanical impacts in liquid oxygen showed that no reactions could be detected in a series of 10 single tests at an impact energy of 750 Nm.

6 Opinion and Interpretation

The product KLINGER Graphit-Laminat SLS-MULTI PLUS, undisclosed batch, shall be used as a sealing material for valves and as a gasket material in flanges on components for gaseous oxygen.

On basis of the test results, the requirements for sealing materials, described in annex 1 to attachment 2 of code of practice M034, annex 2 of code of practice M034-1, Technical Rules for Hazardous Substances TRGS 407 and BAM´s safety philosophy, there are no objections regarding technical safety, to use KLINGER Graphit-Laminat SLS-MULTI PLUS, undisclosed batch, as a sealing material for gaseous oxygen service at following operating conditions:

Maximum Temperature [°C]	Maximum Oxygen Pressure [bar]
60	450
> 60 up to 250	160

On basis of the test results, the requirements for sealing materials, described in annex 1 to attachment 2 of code of practice M034, annex 2 of code of practice M034-1, Technical Rules for Hazardous Substances TRGS 407 and BAM´s safety philosophy, there are no objections regarding technical safety, to use KLINGER Graphit-Laminat SLS-MULTI PLUS, undisclosed batch, as a gasket material with a maximum thickness of 2 mm in flange connections made of copper, copper alloys or steel for gaseous oxygen service at following operating conditions:

Maximum Temperature [°C]	Maximum Oxygen Pressure [bar]
250	160

This applies to flat face flanges, male/female flanges, and flanges with tongue and groove.

Based on the test results, there are also no objections with regard to technical safety to use KLINGER Graphit-Laminat SLS-MULTI PLUS, undisclosed batch, for liquid oxygen service. In this case, a limitation to a particular pressure range is not necessary as compression of liquid oxygen causes no significant change in concentration and therefore has no considerable influence on the reactivity of the material.

7 Comments

This safety-related investigation considers the fact, that on the one hand rapid oxygen pressure changes - so-called oxygen pressure surges – and that on the other hand direct contact of the material with liquid oxygen and mechanical impacts cannot be safely excluded in usage.

This evaluation is based exclusively on the results of the tested sample of a particular batch.

Our experience shows, that the safety characteristics of a product may vary from batch to batch. Therefore, today, we recommend batch testing of products, that are included for oxygen service. In this context, we would like to mention our paper from September 2009: "The Importance of Quality Assurance and Batch Testing on Nonmetallic Materials Used for Oxygen Service", Journal of ASTM International, Vol. 8th; Paper ID JAI102309. This publication can be purchased at www.astm.org.

Products on the market that contain a reference to BAM testing shall be marked accordingly. It shall be evident that only a sample of a batch has been tested and evaluated for oxygen compatibility. The reference shall not produce a presumption of conformity that monitoring of the production on a regular basis is being performed by BAM.

The product may be used for gaseous and for liquid oxygen service. The maximum safe oxygen pressure of the product and its maximum use temperature as well as other restrictions in use shall be given.

Bundesanstalt für Materialforschung und -prüfung (BAM)
12200 Berlin

January 31, 2018

Division 2.1 "Gases, Gas Plants"

By order

Dr. Thomas Kasch

Distribution list:	1. copy:	Klinger AG Egliswil
	2. copy:	BAM - Division 2.1 "Gases, Gas Plants"

Annex 1

Testing for Ignition Sensitivity to Gaseous Oxygen Impacts

Approximately 0.2 g to 0.5 g of the pasty or divided solid sample is placed into a heatable steel tube, 15 cm^3 in volume. In case of liquids to be tested, ceramic fibre, soaked with the sample, is used. The sample tube is connected by a 750 mm long pipe (internal diameter 14 mm) and a pneumatically operated quick opening valve to a high-pressure oxygen accumulator.

A heater allows to set the sample tube to the test temperature t_a After the tube and pipe are at test pressure p_I, the quick opening valve is opened and preheated oxygen of 60 °C and of pressure p_F flows abruptly into the pipe and tube. In this way, the oxygen in the tube and in the pipe is almost adiabatically compressed from pressure p_I to p_F in 17.5 ms ±2.5 ms (according to DIN EN 1797 and ISO 21010) and heated. If there is a reaction of the sample with oxygen, indicated by a steep temperature rise in the tube, further tests with a new sample are performed at a lower pressure ratio p_F/p_I. If, however, no reaction of the sample with oxygen can be detected after a waiting period of 30 seconds, the tube is de-pressurized and the test is repeated (up to four times) until a reaction takes place. This means, each test series consists of a maximum of five single tests with the same material under the same conditions. If no reaction can be observed, even after the fifth single test of a test series, testing is continued with new samples at greater pressure ratios p_F/p_I, until finally that pressure ratio is determined, at which no reaction can be observed within a test series of five single tests.If the repetition of that test series with a new sample shows the same result, the test can be finished or continued at a different test temperature t_a.

Annex 2

Determination of the Autogenous Ignition Temperature in High Pressure Oxygen

A mass of approximately 0.1 g to 0.5 g of the pasty or of the divided solid sample is placed into an autoclave (34 cm^3 in volume) with a chrome/nickel lining. Liquid samples are applied onto ceramic fiber.

The autoclave is pressurized to the desired initial pressure p_I at the beginning of the test A low-frequency heater inductively heats the autoclave in an almost linear way at a rate of 110 K/min. The temperature is monitored by means of a thermocouple at the position of the sample.

The pressure in the autoclave is measured by means of a pressure transducer. Pressure and temperature are recorded. During the test, as the temperature increases, the oxygen pressure increases within the autoclave. The ignition of the sample can be recognized by a sudden rise in temperature and the final pressure p_F.

It is important to know the oxygen pressure p_F, as the autogenous ignition temperature of a material is a function of pressure. It may decrease as the oxygen pressure increases.

Annex 3

Testing for Aging Resistance in High Pressure Oxygen

A sample with known mass is exposed to high-pressure oxygen at elevated temperature in an autoclave for 100 hours. The temperature, at which the sample is aged, is at least 100 °C lower than the autogenous ignition temperature of the sample.

This test shows whether the sample gradually reacts with oxygen or whether it undergoes other visible changes. If there is no change in appearance, in mass, and in the autogenous ignition temperature of the material, it is considered aging resistant.

Annex 4

Testing of Gaskets for Flanges in Oxygen Steel Pipings

The test apparatus mainly consists of two DN 65 PN 160 steel pipes, each approximately 2 m in length, with corresponding standard flanges welded to each pipe.

Both pipes are sealed using the gasket to be tested. In case of a gasket disk its inner diameter is chosen in such a way that it projects into the pipe. If a gasket tape is under test, both ends of the tape are allowed to project into the pipe. The test apparatus is then pressurized with oxygen up to the desired test pressure. The flange is heated by heating sleeves to the test temperature, at least 50 K lower than the ignition temperature of the gasket. An electrical filament ignites that part of the gasket projecting into the pipe. If the gasket is electrically conductive, such as spiral seals or graphite foils, a nonconductive primer capsule of organic material (PTFE, rubber) is used which acts on the seal.

The gasket's behavior after ignition is important for its evaluation. If the seal burns with such a hot flame that the fire is transmitted to the steel of the flange (in most case the test apparatus is destroyed), the seal is considered unsuitable from the beginning. If only those parts of the seal burn that project into the pipe and the fire is not transmitted to the flanges and if the seal does not burn between the flanges there are no objections with regard to technical safety to use the seal under the conditions tested. Such a positive result is to confirm in four additional tests. If, however, the flanged connection becomes un-tight during a test, e. g., because of softening or burning of the seal, the test has to be continued at a lower temperature and oxygen pressure until a positive test result is reached in five tests, as mentioned above.

Annex 5

Testing for Reactivity with Liquid Oxygen on Mechanical Impact

Approximately 0.5 g of the liquid or divided sample is placed into a sample cup (height = 10 mm; diameter = 30 mm), made of 0.01 mm copper foil. Liquid oxygen is poured into the cup over the sample which is then exposed to the mechanical impact of a plummet (mass = 76.5 kg). The drop height of the plummet can be varied. A steel anvil with a chrome/nickel steel plate supports the sample cup. The anvil, having a mass eight times of the plummet, is supported by four damping elements mounted on the steel frame of the test apparatus that rests on a concrete base.

A reaction of the sample with liquid oxygen is usually indicated by a flame and a more or less strong noise of an explosion. The impact energy, at which no reaction occurs, is determined in varying the drop height of the plummet. This result shall be confirmed in a series of ten consecutive tests under the same conditions. The tests are finished, if reactions can be observed at impact energies of 125 Nm or less (equivalent to a drop height of the plummet of 0.17 m or less). In this case, with regard to technical safety, the material is not suitable for liquid oxygen service.