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On the Spontaneous Ignition Temperature of Organic Materials in Oxygen

by

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ON THE SPONTANEOUS IGNITION TEMPERATURE OF ORGANIC

MATERIALS IN OXYGEN

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SUMMARY

Doubts have been expressed on the significance of the current 'Bomb' and 'Pot' tests used to measure the spontaneous ignition temperature of organic materials in high and low pressure oxygen. An investigation by the British Oxygen Company to explore some of these doubts and to test new materials is described and the results are discussed. Suggestions are made for improved 'Bomb' and 'Pot' test procedures, and for investigations into the basic nature of ignition processes and the relationship between laboratory tests and field conditions.

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1   INTRODUCTION

1.1   After several incidents of fire in high pressure oxygen equipment,
which are outlined in Appendix A, the suitability of certain materials for use
in oxygen was reconsidered. Probably the most important physical property
involved is the spontaneous ignition temperature (SIT) of a material in
oxygen.

The main U.K. reference for SITs of materials in high and low pressure
oxygen is the Ministry of Supply Memorandum S & T 13/50 [1], but this report, being
issued in 1950, includes no data on modern materials. Furthermore SITs at
atmospheric pressure were measured by a 'Pot' test whereas a 'Bomb' test was
used at all higher pressures; both tests are detailed in sections 2.1 and 2.2.
Hence the apparent large reduction in SIT which occurs for some materials as
the oxygen pressure is increased from 1 atm to 5 atm and above, could be due,
wholly or in part, to the different methods of test. Some means of correlating
the results of the two tests is obviously desirable.

1.2   In the six incidents leading to this study it was possible that wear by
moving parts could have generated particles of material, or that 'ageing' of
a material either naturally with time, or by contamination, might have occurred.
The effects of these factors on SIT had not been investigated in either the
'Bomb' or the 'Pot' tests. To help clarify the above points an R.A.E. contract
was placed with British Oxygen Company Ltd. to explore the above effects on
the SIT of selected materials; most of which are relatively new and are
intended for use in future oxygen equipment. At about the same time a Mintech
contract was placed with Bristol University, for a paper study of test tech-
niques and means of assessing material compatability with oxygen, which are
currently used in the U.K. and the U.S.A.

1.3   In this Report the two methods of test used by B.O.C. Ltd., the factors
investigated, and the materials tested, are outlined in section 2. The test
results are presented in section 3 and discussed in section 4. The more
fundamental aspects of this work are linked with the work of Bristol
University in section 5. Conclusions and recommendations are given in
section 6.

2   EXPERIMENTAL DETAIL

2.1   British Oxygen Co. Ltd. 'Bomb' test

The high pressure oxygen test, referred to as the 'Bomb' test, is
substantially the same as that used by Guter in 1950 and is fully described

in S & T 13/50 [1]. The 'Bomb' and the associated test apparatus are shown dia-
grammatically in Figs.1 and 2. The temperature in the 'Bomb' is increased at
a·rate of approximately $20^{\circ}C$ per minute and is recorded continuously. Ignition
is indicated by a sudden increase in this temperature.

2.1.1 Use with static gas, pressure in excess of 1 atmosphere

The glass boat, containing a sample of material weighing 60 mg is posi-
tioned in the 'Bomb' so that it is directly beneath the thermocouple tip,
midway along the heating element. The nose plug is tightened into the 'Bomb'
chamber which is then purged with oxygen at 5 atm pressure. The chamber is
then filled with oxygen to approximately 90% of the required test pressure.
Heating is commenced and the temperature recorded. The pressure increases with
the temperature, and any excess gas is vented through a manually operated
valve in the outlet pipe.

When either ignition occurs, or a temperature of $400^{\circ}C$ is reached, the
heating is switched off. After the system has cooled to $100^{\circ}C$ the gas is
vented and the test sample examined.

2.1.2 Flowing gas at 1 atmosphere pressure

A weighed sample is positioned in the 'Bomb' as above. A flowmeter is
then connected to the outlet and the flow adjusted to either 0.2 1/min or
2.0 1/min. The meter is then disconnected, but the constant mass flow of
oxygen is maintained and is vented to a fume cupboard. The heating is then
switched on and the experiment continued as above.

2.2 British Oxygen Co. Ltd. 'Pot' test

A diagram of the test apparatus, which is fully described elsewhere[1]
is given in Fig.3. The temperature of the oxygen in the open ended tube or
'Pot' is maintained at a predetermined value to within $\pm 2^{\circ}C$ for 15 minutes.
A sample of material, weighing 60 mg is placed on a Pyrex glass spoon and is
then lowered into the gas stream. If no ignition is seen within two minutes
the test is repeated with a fresh sample of material. Samples are tested for
gas temperature increments of $5^{\circ}C$, either until ignition occurs or until a
temperature of $400^{\circ}C$ is reached.

2.3 Outline of investigation

2.3.1 Aims

The materials and the test conditions were chosen in order to investi-
gate the following factors:

(i)   The spontaneous ignition temperature of nylon, and of the sealing compound ZX32: both of which were suspect materials in recent fire incidents.

(ii)   The effect of 'ageing', either with time or by contamination, on the spontaneous ignition temperature of nylon used in R.A.F. line valves.

(iii)   The comparison of the results of the 'Bomb' and the 'Pot' tests, both at atmospheric pressure, (see section 1.1).

(iv)   The difference in SIT between powdered samples and block samples of equal weight of the same material.

(v)   The spontaneous ignition temperature of the materials listed in section 2.3.3, most of which are relatively new and are intended for use in future equipment. These materials were chosen after consultation with several firms which have design and/or production contracts from Mintech HQ.

2.3.2 Test schedule

The conditions of each test are detailed in the results shown in Figs.4, 5 and 6 and are outlined below:

SIT of materials measured by 'Pot' test

60 mg block samples of each material, listed in section 2.3.3 were tested at atmospheric pressure with an oxygen flow rate of 2 1/min. 60 mg powdered samples of each solid material were also tested in the same conditions. The required number of samples to establish the ignition temperature, or to reach the $400^{\circ}C$ temperature limit of the apparatus, were used. The SIT was 'established' when the first three samples tested at one temperature, all ignited.

SIT of materials measured by the 'Bomb' test

Six 60 mg block samples of each material listed in section 2.3.3 were tested in static oxygen at 10 atm and 130 atm above atmospheric pressure, as these are the working pressures of aircraft LOX and high pressure gas systems respectively. Some of the materials were also tested at 5 atm and 50 atm above atmospheric pressure. Six 60 mg powdered samples of each solid material were also tested under the same conditions as the block samples.

So that the 'Bomb' and 'Pot' tests could be compared, 60 mg samples, in block and powder form of most materials, were tested in the 'Bomb' at 1 atm pressure in flowing gas. A flow of 2 1/min was used to give the same mass flow as in the 'Pot' test. Because of differences in the sizes of the two test

apparatuses, some tests were repeated in the 'Bomb' with a flow of 0.2 l/min, so that the gas velocity was the same as in the 'Pot' test.

2.3.3 Classification of materials

The materials tested fall into four main groups:

Group A - Nylon

    (i)   New Nylon 66.

    (ii)   Used Nylon 66 (valve seats of high pressure line valves removed from R.A.F. aircraft because of stripped threads etc.).

    (iii) A new type of nylon designated B100.

Group B - Lubricants and sealing compounds

    (i)   Rocol MA-1 (water based, molybdenum disulphide with organic soap).

    (ii)   Rocol dry film lubricant (water based, molybdenum disulphide, sodium silicate).

    (iii) Acheson Industries Ltd. ZX32 (DAG517. A suspension of graphite in a non-flammable fluid).

    (iv)   Silicone grease XG315 (equivalent to MS33).

Group C - Elastomers and thermoplastic materials

(i)	ICI, silicone rubbers (room temperature vulcanised)	Silcoset 100 Silcoset 106
(ii)	Midland Silicones Ltd., silicone rubbers	Silastomer S2453 Silastomer S2475
(iii)	Dow Corning, silicone rubber	Silastic 55
(iv)	J. Walker & Co. Ltd., (PTFE molybdenum disulphide fibre glass mixture).	Fluolion G15M

Group D - Adhesives

(i)	Midland Silicones Ltd., silicone adhesive	MS2705
(ii)	Douglas Kane Ltd., shaft locking compound.	Loktite D.

2.3.4 Preparation of materials

All samples as received from the suppliers were handled with clean, oil free tools. Block samples were cut into 60 mg portions using clean degreased cutters. Powders were made by means of a new degreased file cooled in liquid nitrogen. A separate file was kept for each material to prevent cross contamination. Only that portion of the powder which would pass through a size 30 mesh, but not through a size 85 mesh was used in the tests as this was thought to be representative of the size of particle which could be formed inside valves etc. by general wear. One exception was however made: because only a limited supply of used nylon was available the powder was graded by size 30 and size 200 mesh for this material only.

3   RESULTS OF TESTS BY THE BRITISH OXYGEN CO. LTD.

The spontaneous ignition temperature of each sample of material is shown diagrammatically in Figs.4, 5 and 6. Detailed results of 'Pot' tests, illustrating test procedure, are given in Fig.7. A summary is given in Table 1.

The most noticeable features of the results are:

(i)   The wide range of measured SIT for certain nominally identical sample and test conditions, especially in the 'Bomb' test.

(ii)   The low SIT of some powdered 'aged' samples of nylon.

(iii)   The increase in the SIT of several silicone materials with increasing oxygen pressure.

Wherever possible a statistical analysis has been made to assess the significance levels of the effects of various factors on SIT. Details of the analysis are given in Appendix B and the results presented in Tables 2 to 6. As some of the results were indefinite, being stated as 'above $400^{\circ}C$' the validity of the findings is uncertain, but some trends, summarised in the table on the following page are apparent.

Test	Material	Factor giving lowest statistically significant SIT	Factor giving lowest individual SIT
Comparison of 'Pot' at 2.0 1/min and 'Bomb' at 0.2 and 2.0 1/min 1 atm.	Silicones Loktite D	'Bomb' 'Pot'	'Bomb' 'Bomb'
Comparison of flow rates in 'Bomb' test	Silicones Loktite D	High flow No significant difference	High flow Low flow
Effect of pressure on 'Bomb' test	Silicones (not XG315) XG315 and Nylon Loktite D	Low pressure High pressure Low pressure	Low pressure High pressure Low pressure
Comparison of block and powder 11 atm static 11 atm static 1 atm flowing 51 atm static 131 atm static	 Silicones Nylon Silicones Nylon Nylon	 Block Block Powder Powder Powder	 Block Block Powder Both same Powder
Effect of age and use	Nylon	Used material	Used material

4 DISCUSSION OF BRITISH OXYGEN CO. LTD.'S RESULTS

It is apparent that the nature of the test, whether 'Bomb' or 'Pot', static gas or flowing gas, and that the condition of the test sample, whether in block or powder form, new or used, can considerably affect the SIT of a material. However no generalizations regarding the differences between 'Bomb' and 'Pot' tests, or block and powder samples, can be made. For instance most silicone materials have a lower SIT in the 'Bomb' at atmospheric pressure, than in the 'Pot' at atmospheric pressure. The reverse is true for three powdered samples of nylon, and for Loktite D when the flow through the 'Bomb' is 2 1/min, these materials do not contain silicone. Similarly powdered materials may have either a higher or lower SIT than blocks of materials, depending upon the oxygen pressure. Additionally nominally identical tests on six samples yielded a wide range of SITs in some cases; and the results of the 'Bomb' test at 1 atm varied significantly with the velocity of oxygen. These factors are discussed separately in the following sections.

4.1 Spread of results

An interesting and so far inexplicable feature of the 'Bomb' test results which does not occur with those of the 'Pot' test is the wide range of measured values for certain nominally identical conditions. It is presumed that generally the SIT of a material is measured for comparison with some predetermined lowest limit of acceptability, and hence some method of interpreting the spread of results is needed. If the distribution of SITs about the mean value is random, then 95% of all samples of material can be expected to have an SIT within two standard deviations of the mean measured SIT, hence 97½% will have an SIT above the 'mean minus two s.ds' temperature.

It is therefore suggested that if the mean SIT minus two standard deviations, is equal to or greater than a specified critical temperature, then the material is acceptable. With this mode of interpreting the results there is a 2½% or less probability that the actual SIT of any single sample falls below the acceptance level.

Although 2½% might at first sight seem to be high, it must be remembered that first this probability of a sample having an SIT less than the predetermined lowest acceptable value will apply only to borderline materials; it is expected that many materials will have SITs much higher than the critical temperature in which cases any risk will be negligible.

Secondly, if a material only just passes the acceptability test then for a fire to occur the 2½% or less of items having SITs less than the critical temperature must coincide with an occurrence of abnormally high temperature. As normal precedures for using oxygen equipment are designed to prevent such occurrences, high temperatures are expected to be rare, hence the probability of fire, even with borderline materials, should be very much less than 2½%.

4.2 Ageing of nylon

The results (Table 2) indicate that the SIT of nylon can significantly decrease over a period of time in use in a high pressure oxygen system. The exact cause of this reduction is not known, but it is suggested that either the nylon undergoes some physical or chemical change when used continually in high pressure oxygen, or small amounts of contamination build up on the surface of the nylon: the ignition of such contaminants could release sufficient energy to ignite the nylon. Both of these suggested mechanisms have received limited study in the U.S.A. One investigator[2] showed that after prolonged storage in oxygen some materials are degraded physically and chemically,

however, no measurement of resultant SIT was attempted. Another investigator[3] showed that, as would be expected, material of high SIT can be ignited if a material of low SIT burns on its surface, and a 'promoted ignition test' based on this mechanism, was devised.

This ageing effect was probably a contributory cause to some of the fires listed in Appendix A.

4.3   New materials

The increase in the SIT with increase in oxygen pressure of all except one silicone material is the reverse of the findings of 1950[1] for materials not containing silicone. This, together with the fact that the lowest SIT was 300°C indicates that wider use of silicone materials could be encouraged in high pressure oxygen systems. However, only limited tests have been performed and the effect of ageing has not been investigated. More comprehensive tests would be needed before any definite conclusions could be reached.

4.4   Effect of powders

As can be seen in Table 3 some materials which can be powdered give significantly different SITs in the powder form than in block form. However, the effect of powdering varies amongst materials and for a given material, depends upon test technique and oxygen pressure. No consistent pattern of behaviour could be found, nor could the change of SIT with powdering be explained. As particles of a material could be produced in manufacture and assembly, or in use, then the change of SIT with powdering can considerably affect the overall compatibility of the material with oxygen systems. Tests of material compatibility with oxygen should therefore include the SIT of both block and powder samples (section 5.2).

The reduction in SIT at high pressure, of 'aged' nylon, due to powdering may have been a contributory factor to the fires which sparked off this investigation.

4.5   Comparison of 'Bomb' and 'Pot' tests

From Figs.4, 5 and 6 it can be seen that, with the exception of one sample of nylon, the measured SIT of all solid materials was lower in the 'Bomb' at 1 atm than in the 'Pot' at 1 atm. Similarly for lubricants, sealants and adhesives, although the statistical analysis detailed in Table 4 shows no significant differences, there is some indication that the 'Bomb' gives lower

measured SITs than does the 'Pot'. Hence, the apparent large reduction in SIT
of some materials, which was noted in S & T 13/50 [1] as the pressure increases
from 1 atm in the 'Pot' to higher pressures in the 'Bomb', can be attributed,
in part, to change in test technique. Hence when comparing materials for
compatibility with oxygen, effects of test technique cannot be neglected.

The conditions of the 'Bomb' and 'Pot' tests are compared with one
another, and with actual conditions from which a fire might arise, in Table 5.
The two major differences at atmospheric pressure are flow rate and heating
rate. From Figs.4, 5 and 6 and Table 5 it will be noted that a change of flow
rate in the 'Bomb' can cause a change in measured SIT; for solids a decrease
in SIT accompanies an increase in flow rate, but for lubricants, sealants and
adhesives an increase in flow rate causes an increase in SIT. Although the two
flow rates in the 'Bomb' were chosen to give either the same gas velocity or
the same mass flow as in the 'Pot' test, neither set of 'Bomb' test results at
1 atm correlated with the 'Pot' test results.

Some of the differences could be attributed to the wide difference in
heating rates. Whereas in the 'Pot' tests a material is lowered into hot gas
and a relatively rapid rate of heating ensues, in the 'Bomb' test the material
and the 'Bomb' are heated simultaneously and slowly. Thus in the 'Pot' there
is little opportunity for gaseous material to evolve and accumulate at a sample
temperature below that of the gas, but in the 'Bomb' test there is ample
time for vapours to be generated and accumulated, and a combustible mixture
might be formed and ignited at a temperature lower than the 'Pot' ignition
temperature. Also it is possible that during the 20 minute heating period in
the 'Bomb' some of the evolved vapours decompose to materials which have SITs
different from the SIT of the original vapours. Such vapours might have a
lower or higher SIT than the original vapour and could accelerate or inhibit
the onset of fire. Alternatively, slow heating might produce slow, but not self
sustaining, ignition which could lead to the test sample being surrounded by a
layer of incombustible vapour.

Accumulation of vapour during the heating process can be affected by the
rate of flow of oxygen through the apparatus, as high flows will tend to sweep
away any vapour. In the 'Pot' test it is expected that, because of rapid heating
and relatively fast flow rates, any evolved vapour will be swept away rapidly,
very little decomposition will occur and only when a high temperature is
attained will combustion occur. However, in the 'Bomb' the sweeping away of

any vapour would remove either ignitable material or inhibitors, thus increasing the flow rate of oxygen would in the first case increase the SIT by removing ignitable vapour, and in the second case reduce SIT by removing an inhibiting blanket of vapour. The former might apply to Loktite and silicone adhesive, the latter to silicone grease, Silicoset 100 powder, and Silastic 55 powder.

Obviously the above discussion is conjectural and there is relatively little data on the increase or decrease of SIT with flow rate. Equally obviously the 'Bomb' and 'Pot' tests cannot be correlated, nor is there any ready general explanation of the differences. Hence the 'Pot' test alone, which rarely gives the lowest SIT at atmospheric pressure, is not suitable for assessing the behaviour of a material at 1 atm or at higher oxygen pressures. Additionally as shown in Table 5, neither test fully represents the nature of ignition processes which are likely to occur in oxygen systems. As these two tests are generally accepted in the U.K. as the standard means of measuring SIT and hence of assessing material compatibility with oxygen, then further study of these, and other test techniques is desirable.

5   FURTHER CONSIDERATIONS OF MATERIAL COMPATIBILITY WITH OXYGEN

When choosing a material for use in oxygen the overriding question, once mechanical suitability and absence of toxic hazards and odour have been established, is whether or not the material is a fire hazard. This problem is generally resolved in the U.K. by measuring the SIT of the material using the 'Bomb' and 'Pot' test methods. But, as shown in section 4.5 the results of these two tests can be widely and inexplicably different, and, as illustrated in Table 5 neither test fully represents actual ignition processes. Despite this no other standard test or set of tests, by which to measure material compatibility with oxygen, in respect of fire prevention, is known to exist in the U.K. Clearly some such test is desirable. However, the work reported here, and the investigation made at Bristol University indicate that a considerable amount of basic work would be necessary before a standard laboratory test could be established and correlated with field conditions.

5.1   Basic work

There are four major parameters which are thought to affect ignition of material, and which would need investigating.

(i)   The temperature, often localised, of the material and its immediate surroundings.

(ii)   The chemical condition of the material, e.g. surface oxide layer.

(iii)   The physical condition of the material, e.g. surface contamination, block or powder for solids, thick or thin layers for liquids.

(iv)   The oxygen pressure.

The first three of these parameters are thought to be controlled by:

(v)   The energy involved in the triggering process, e.g. friction, impact, etc.

(vi)   The rate of application of energy.

(vii)   The gas flow round the material which can remove unignited vapour or products of combustion, and can affect local temperatures.

(viii) The specific heat of the material and its surroundings.

(ix)   The thermal conductivity of the material and its surroundings.

(x)   The thermal absorption and emission characteristics of the material and its surroundings.

The extent and seriousness of the propagation of fire depends upon many of the above factors and also on:

(xi)   The calorific value of the material.

Any basic work on these factors would almost certainly need to be related to the conditions likely to occur in actual oxygen systems.

5.2   Interim standard test

Any study as outlined above would be complex and lengthy. It is therefore suggested that an interim standard test should be adopted. Although the 'Pot' test gives results which are more consistent than those of the 'Bomb' test it is usable only at 1 atm pressure and there are no reliable means of extrapolating the results to higher pressures. Also in most, but not all, cases, the 'Pot' SIT is higher than the 'Bomb' SIT; and it is the lowest measured SIT which is particularly important in assessing material compatibility with oxygen. It is therefore suggested that the 'Pot' test, and a modified 'Bomb' test both be used as interim standards, new materials being tested over a full range of conditions and subsequent quality control tests being made for only a few selected conditions, namely those for which the material has its lowest SIT.

The range of initial test conditions for the interim standard test should include:

(i) (a) Block and powder samples for a solid.

(b) Thick and thin films for a liquid or grease.

(ii) Oxygen pressures of 0, 4, 9, 49 atm above atmospheric pressure and then at 50 atm intervals up to the maximum working pressure of the material, in the 'Bomb' test, atmospheric pressure in the 'Pot' test.

(iii) A realistic range of flow rates of oxygen.

(iv) A range of sample heating rates.

Wherever this test shows that two materials appear equally suitable then the one with the lowest calorific value should be used, as this material would be least likely to ignite, or to propagate ignition if contamination having a lower SIT caught fire, the violence of any fire will therefore be minimum.

Unpublished work at R.A.E. has shown that when a manually operated valve is suddenly opened, so allowing high pressure gas to enter a closed region which was initially at low pressure, transient temperatures up to $300^{\circ}C$ can be attained. As such sudden temperature increases could occur in actual oxygen systems, item (iv) above might include sudden insertion of a sample into a pre-heated 'Bomb'. However, as the 'Pot' test showed that sudden heating of a sample at 1 atm tends to give higher SITs than the slower heating rates of the 'Bomb' test, and as rapid insertion of samples would necessitate modification of existing 'Bomb' test apparatus, it is thought that item (iv) could be limited to those heating rates currently obtainable with existing apparatus.

In view of the compression temperatures measured at R.A.E. it is suggested that the critical ignition temperature for assessing material compatibility with medium and high pressure oxygen should be at least $300^{\circ}C$. Any material which might ignite below this temperature in normal working conditions, should be deemed to be incompatible with oxygen in those conditions. Spread of experimentally measured SITs should be interpreted as suggested in section 4.1, that is, if the mean measured SIT, minus twice the standard deviation of the measured SITs is above the critical temperature ($300^{\circ}C$) for all proposed working conditions, then the material is compatible with oxygen.

6   CONCLUSIONS AND RECOMMENDATIONS

(1) The dependence of the spontaneous ignition temperature, SIT, of a material on test techniques such as heating rate and gas flow rate, and on sample conditions such as powder or block, new and clean or used and 'aged', has been demonstrated; but no consistent trends were apparent (sections 4.1 to 4.5).

(2) Previously reported large decreases in SIT with increase in pressure above atmospheric are likely to have been partly caused by the change in test technique (section 4.5). With few exceptions the 'Pot' test gives higher SITs than the 'Bomb' test, hence the use of the 'Pot' test alone, to assess the suitability of materials for use in oxygen, cannot be recommended.

(3) Nylon is not recommended for use in high pressure oxygen. Even when new or unused its SIT can be below $300^{\circ}C$ (section 3), and wear and 'ageing' during use can apparently lower the SIT to $155^{\circ}C$ (section 4.2). These could have been contributory factors to the six fires from which this investigation stemmed.

(4) ZX32 a material suspected in one fire, did not ignite in any test.

(5) The SITs of several relatively new silicone materials have been measured and generally increase with an increase in oxygen pressure (section 4.3 and Fig.5). As this is the reverse of the behaviour of many non-silicone materials tested in 1950[1], silicone materials might well be used more widely in high pressure oxygen systems. However, only limited tests have been made so far: further investigation would be necessary before any definite conclusions could be drawn.

(6) The need for a test or set of tests by which to define the compatibility of a material with oxygen has been discussed (section 5) and a programme of work aimed at establishing such a test has been outlined (section 5.1). An interim standard test has been proposed (section 5.2) and a method of interpreting any spread of results suggested (sections 5.2 and 4.1).

ACKNOWLEDGEMENTS

Appendix A

FIRES/EXPLOSIONS IN OXYGEN VALVES

A.1   1962

A high pressure oxygen bottle was opened to a short length of pipe, terminated by a valve which contained a nylon gland and seat. The oxygen supply was part of a kerosine test rig. The valve 'exploded' and burned.

A.2   1965

The oxygen charging valve of a Hastings aircraft 'exploded' 20 seconds after the ground trolley valve had been opened. The valve body was burned through at the position of the nylon seat, and the pipe on the aircraft side of the valve was extensively damaged. The nylon gland and the end of the stainless steel spindle were destroyed.

A.3   1966

The charging valve of a Jet Provost aircraft 'exploded' about 3 minutes after a slow charging procedure had been commenced. Extensive damage was suffered by the valve and its mounting bracket, particularly at the position of the valve seat, which was either nylon or PTFE. All the charging valves of the 22 aircraft on the servicing line were replaced and the removed valves examined; three were found to have dark deposits on the valve seat. Limited analysis of the small quantity of contamination available indicated that it consisted of small pieces of iron, coated in oxide, together with nylon.

A.4   1966

50 seconds after the master on-off valve of a test-rig in an oxygen-clean area had been turned on, a hissing noise was heard. 20 seconds later the valve exploded whilst being turned off. The valve burned vigorously in the free flowing oxygen and was reduced to a shapeless mass of material. The pipe upstream of the valve and all the surrounding area was severely damaged. The valve which had a nylon seat had been in the test-rig since 1963.

A.5   1967

A nylon seated valve exploded with a flash shortly after 1250 psi oxygen had been released into a closed pipe at 15 psia. The valve was in a commercial air/oxygen chamber. Contamination in the pipe line was suspected.

A.6   1967

    When a valve in a portable oxygen set stuck in the open position it was
removed and dismantled. It was found that part of the nylon gland and several
threads of the stainless steel spindle had burned. The glass loaded PTFE seat
had disintegrated but the small remaining particles showed no signs of
ignition.

NB   Several years ago the manufacturer of several of the valves above realised
the potential hazards of nylon and redesigned the valve to eliminate nylon.

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Appendix B

STATISTICAL ANALYSIS OF RESULTS

The results for each material were examined for differences caused by:

(1) Different flow rates in the 'Bomb' at 1 atm.

(2) Block and powder samples.

(3) 'Bomb' and 'Pot' tests.

(4) Oxygen pressure.

In addition the results with nylon were tested for changes in SIT caused by:

(5) 'Ageing' during use.

For some conditions, particularly increasing oxygen pressure, the effect on SIT was obvious. For other conditions where the spread of sample results overlapped, Student's 't-test' was used to find the significance level of the difference between sample means.

t-test

For two samples of mean $\bar{x}_1$ and $\bar{x}_2$ and individual values $x_{11}, x_{12}, \ldots x_{1n}$ and $x_{21}, x_{22}, \ldots x_{2m}$ the value of t is given by:-

$$t = (|\bar{x}_1 - \bar{x}_2|) \left(\frac{X_1^2 + X_2^2}{n + m - 2} \cdot \frac{n + m}{n.m} \right)^{-\frac{1}{2}}$$

where

$$X_1^2 = \sum_{r=1}^{r=n} (x_{1r} - \bar{x}_1)^2$$

$$X_2^2 = \sum_{r=1}^{r=m} (x_{2r} - \bar{x}_2)^2$$

$$\bar{x}_2 = \sum_{r=1}^{r=m} \frac{x_{2r}}{m}$$

the calculated value of t is then compared with the tabulated values to find the significance level which is tabulated as a per cent point.

A $y\%$ point means that for a large number of random paired samples of one population the particular value of t would occur $y\%$ of the time: that is, there is $(100 - y)\%$ probability that the two samples are from different populations. The 5% point (95% probability that the samples represent different populations) is generally accepted as being significant. The 1% point is very significant, and at the 0.1% point it is virtually certain (99.9% chance) that the two samples came from different populations.

The t-test depends on the two samples having the same standard deviation. This can be tested by the F-test:

$$F = \frac{x_1^2}{x_2^2} \cdot \frac{m - 1}{n - 1}$$

by consulting tables the significance level of the calculated value of F can be found. For any per cent point larger than 5 it is generally accepted that there is no significant difference in the standard deviation.

Method of application

In comparing two samples A and B each with six values, where the results of A are all above 400°C, then the value of x^2 for A has been assumed to be equal to that of B, and the mean of A equal to $400 + (1$ standard deviation B). Where a few values of a sample were above 400°C then assumed values of 410°C for the first and 420°C for the second, were used. This latter assumption was thought to be reasonable in view of the spread of most results. The use of one approximation precluded the use of the other.

In comparing the 'Bomb' and 'Pot' tests the range of values for each was obviously different; that is, F was highly significant and hence any t-test would be invalidated. However, for most materials the two tests gave obviously different results: where this is not so the test giving the lowest individual SIT is quoted. In all other comparisons F was not significant.

For otherwise identical test conditions, pairs of batch samples, each batch having 6 values, were tested for differences caused by:

(1) Block and powder.

(2) Oxygen flow rate; 0.2 and 2.0 l/min in the 'Bomb' test.

(3) Ageing of nylon.

The results are given in Tables 2, 3, 4 and 6.

Table 1

RANGE OF SPONTANEOUS IGNITION TEMPERATURES, °C, OF MATERIALS IN OXYGEN

Material	'Pot' test 2 l/min 1 atm	'Bomb' test			
		2 l/min 1 atm	0.2 l/min 1 atm	Static 11 atm	131 atm
Nylon 66					
New block	395 to >400	>400	>400	335 to 385	285 to 315
New powder	>400	>400	>400	>400	275 to 310
6 year old block				290 to >400	275 to 360
4–6 year old powder*				355 to >400	215 to 270
1–5 year old block				300 to 320	250 to 320
Up to 7 year old powder*				350 to >400	155 to 315
Nylon B100					
New block				335 to >400	305 to 355
New powder				355 to >400	265 to 350
Silcoset 100 block	>400	370 to >400		320 to 370	>400
Silcoset 100 powder	385	315 to 355	345 to 400	355 to 375	>400
Silcoset 106 block	>400	>400		>400	>400
Silcoset 106 powder	>400	>400		· >400	>400
Silastomer S2453 block	>400	>400		305 to 395	>400
Silastomer S2453 powder	380 to 395	305 to 320		360 to 370	>400
Silastomer S2475 block	400	360 to 400		335 to 375	>400
Silastomer S2475 powder	375	295 to 310		345 to 355	380 to >400
Silastic 55 block	>400	>400	>400	365 to 380	>400
Silastic 55 powder	>400	345 to 370	375 to 395	370 to 385	>400
Fluolion block	>400	>400	>400	>400	>400
Fluolion powder	>400	>400	>400	>400	>400
Rocol MA-1					305 to 330
Rocol dry film lubricant	>400	>400	>400	>400	>400
Silicon grease XG315	>400	375 to 400	>400	275 to 355	255 to >400
Sealing compound ZX32	>400	>400	–	>400	>400
Silicon adhesive MS2705	340 to 345	290 to >400	345 to >400	290 to 360	310 to 330
Loktite D	220 to 230	>400	190 to >400	170 to 210	230 to 280

* Powder graded by mesh sizes 30 and 200; all other powders graded by mesh sizes 30 and 85.

Table 2

EFFECT OF AGEING ON SIT OF NYLON

Material condition	6 atm oxygen	11 atm oxygen	51 atm oxygen	131 atm oxygen
Block	4-6 year old 0.1% level	no significant difference	4-6 year old 0.1% level	New 1.0% level
Powder	4-6 year old 10% level	4-6 year old 5% level	4-6 year old obvious significant difference	4-6 year old 1.0% level

The condition giving the lowest SIT, and the significance level of the difference in SITs of new and 'aged' material are given.

Note that a '1% level' means that there is a 99% chance that the two conditions cause different SITs.

Table 3

SIGNIFICANCE LEVELS OF DIFFERENCES BETWEEN SITs OF BLOCK AND POWDER SAMPLES

Material	'Pot' test	'Bomb' test					
		2 1/min	0.2 1/min	6 atm	11 atm	51 atm	131 atm
Silcoset 100	OS	+0.1%	–	–	NS(B)	–	NS
Silcoset 106	NS	NS	–	–	NS	–	NS
Silastomer S2453	OS	+0.1%	–	–	NS(B)	–	NS
Silastomer S2475	OS	+0.1%	–	–	NS(B)	–	NS(P)
Silastic 55	NS	+0.1%	+1%	–	-5%	–	NS
Fluolion	NS	NS	NS	NS	NS	NS	NS
New Nylon 66	NS(B)	NS	NS	NS(B)	-1%	NS(B)	NS(P)
6 year old Nylon 66	–	–	–	-0.1%	NS(B)	+2%	+0.1%
New Nylon B100	–	–	–	-5%	NS(B)	+1%	NS(P)

KEY   NS   not significant   OS   obvious significant difference

    +ve   block SIT higher than powder SIT   –ve   block SIT lower than powder SIT

    (P) or (B)   either powder or block gave
                lowest individual SIT

NOTE: A '1% significance level' means that there is a 99% chance that block samples
       have different measured SITs from powdered samples.

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Table 4

COMPARISON OF 'BOMB' AND 'POT' TESTS

Material	Test giving lowest SIT and significance level	
	'Pot' 2 1/min ⎫ same gas 'Bomb' 2 1/min ⎭ flow rate	'Pot' 2 1/min ⎫ same gas 'Bomb' 0.2 1/min ⎭ velocity
Silcoset 100 block	2.0% 'Bomb'	–
powder	0.1% 'Bomb'	5% 'Bomb'
Silastomer S2435 powder	obvious 'Bomb'	–
Silastomer S2475 powder	obvious 'Bomb'	–
Silastic 55 powder	obvious 'Bomb'	0.1% 'Bomb'
Silicone grease XG315	no significant difference	–
Silicone adhesive	no significant difference	no significant difference
Loktite D	obvious 'Pot'	no significant difference

Note A '1% significance level' means that there is a 99% chance that the
'Bomb' and 'Pot' tests give different SITs.

Table 5

COMPARISON OF 'BOMB' TEST AND 'POT' TEST CONDITION WITH
ACTUAL SITUATIONS

Factor	'Bomb' test	'Pot' test	Actual situations
Method and extent of heating	All round heating by conduction convection radiation	All round heating by conduction convection radiation	All round heating from external sources by conduction convection radiation and/or locally generated heating by partical impact friction gas resonance electrostatic discharge.
Rate of heating	Slow approx 20°C/min	Moderately fast approx 200°C/min	Very fast to very slow.
Oxygen flow rate	0 1/min (usually)	2 1/min (usually)	Large flow range, upwards of 0 1/min.
Oxygen pressure	Any	1 atm	Any
Condition of test material	New block or fluid	New block or fluid	New or 'aged' block or small particles or fluid.

Table 6

EFFECT OF FLOWRATE ON 'BOMB' SIT

Material	Flowrate giving lowest SIT	Significance level
Silastic powder	2.0 1/min	0.1%
Silcoset 100 powder	2.0 1/min	5%
Adhesive MS2705	-	No significant difference
Loktite D	0.2 1/min	Obvious significant difference

Note A '1% significance level' means that there is a 99% chance that
the two flowrates cause different measured SITs.

REFERENCES

No.	Author	Title, etc.
1	M. Guter	Ignition in high pressure oxygen. Ministry of Supply S & T 13/50 (1950)
2	J. V. Baum B. Goobich T. M. Trainer	An evaluation of high pressure oxygen systems. AMRL-TDR-62-102 (1962)
3	G. J. Nihart C. P. Smith	Compatibility of materials with 7500 psi oxygen. AMRL-TDR-64-76 (1964)
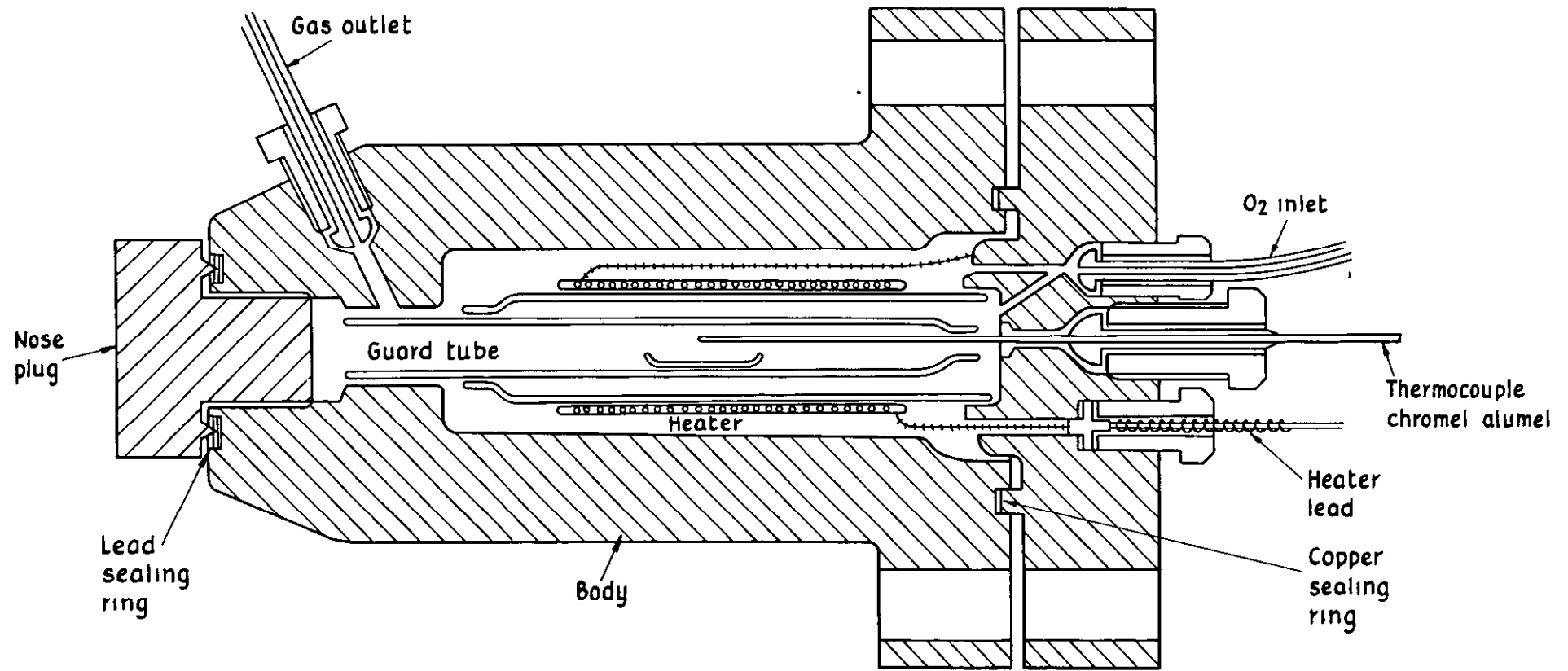
Fig.I High pressure bomb assembly
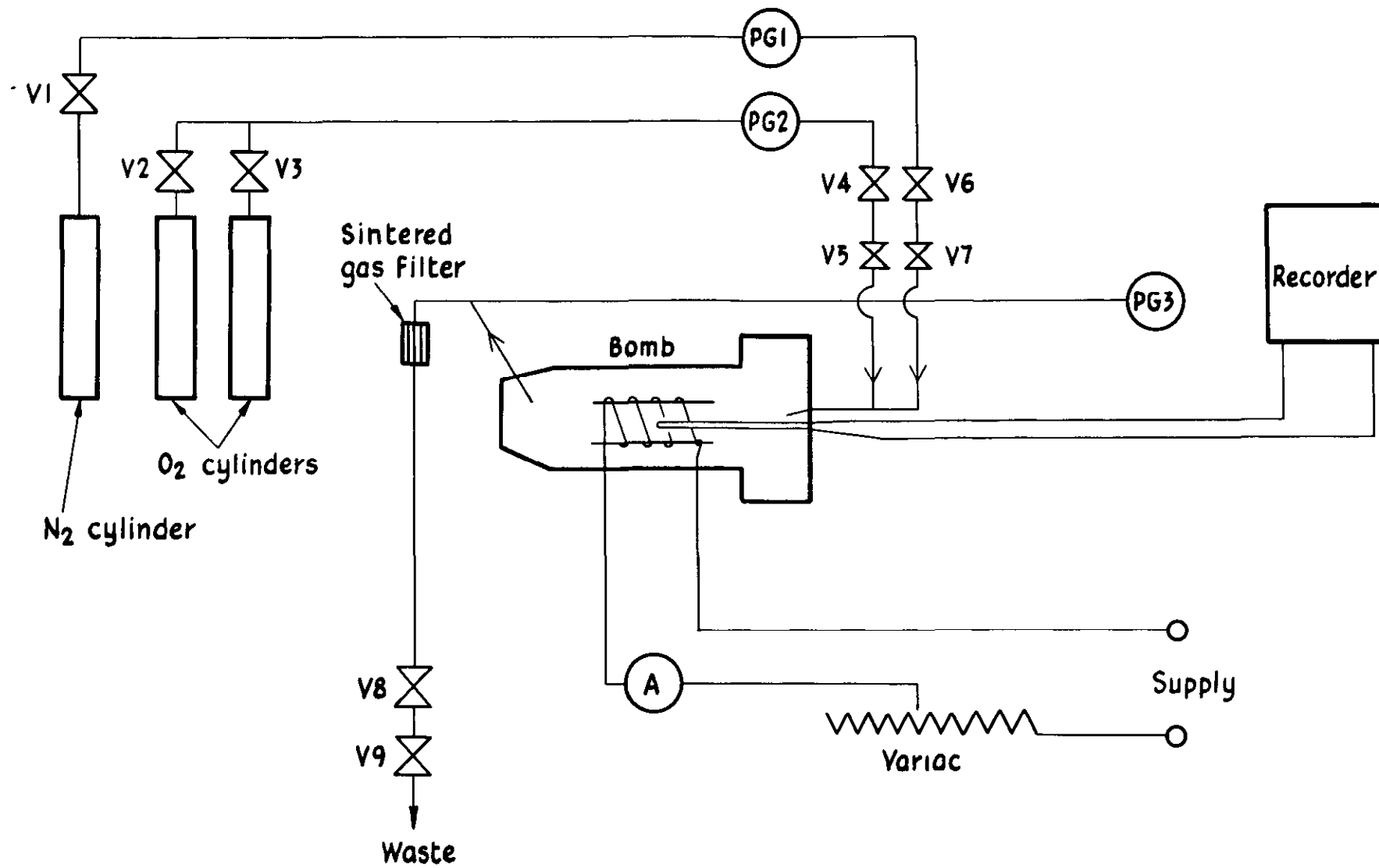
Fig. 2 Flow sheet for H P ignition apparatus
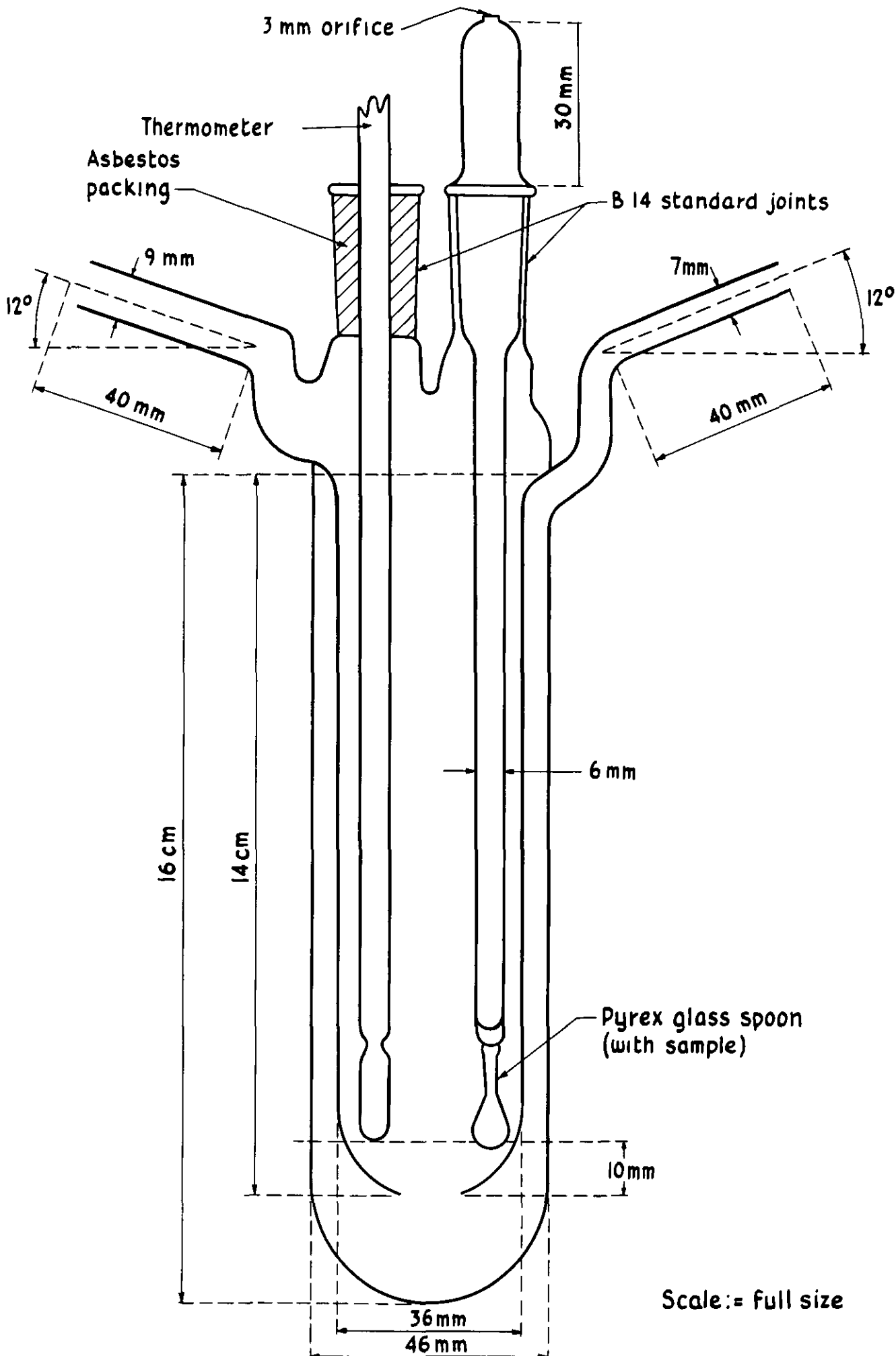
Fig.3 Apparatus for ignition tests ('pot')
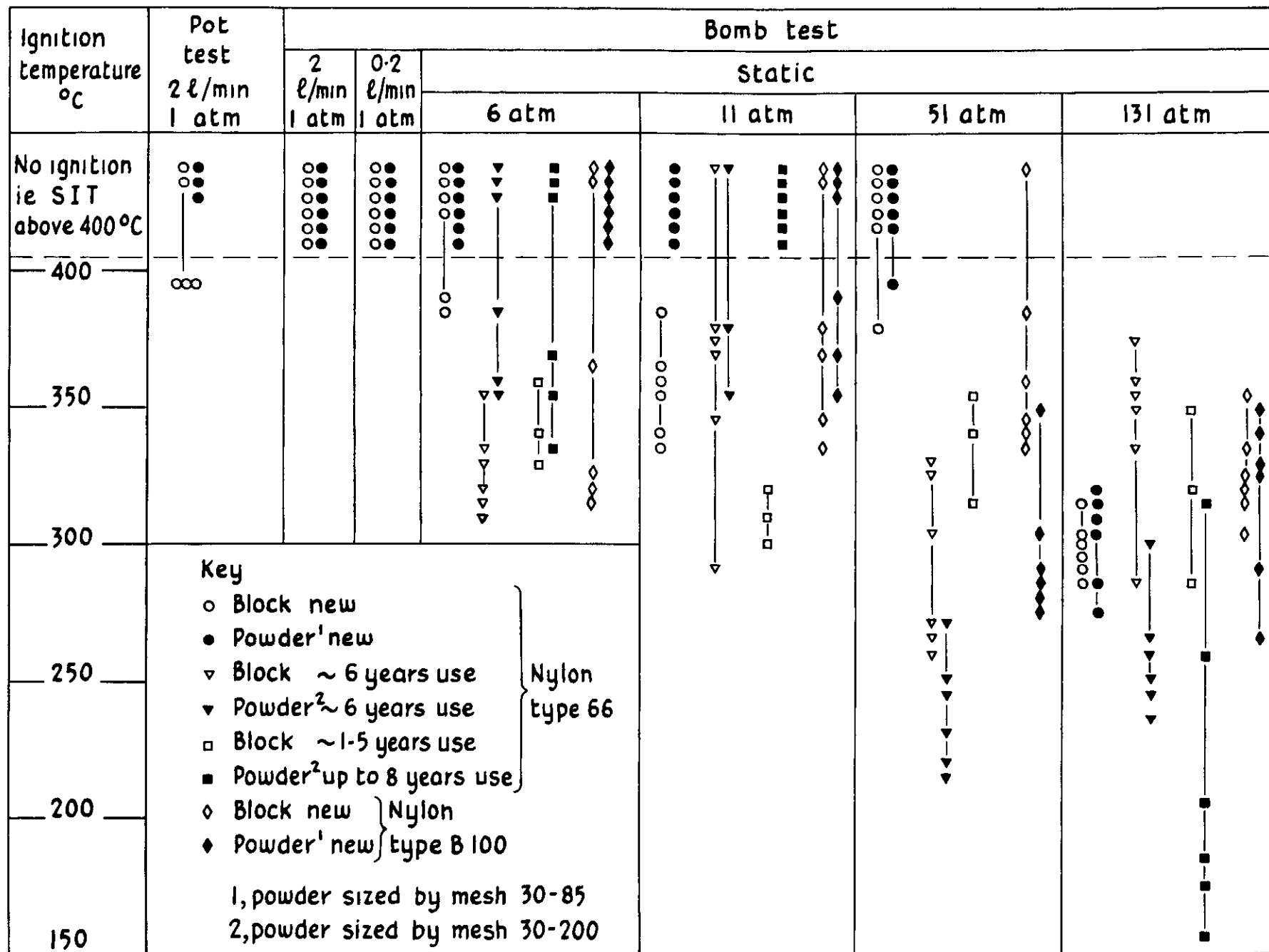
Fig. 4 Spontaneous ignition temperatures of new and used nylon in oxygen
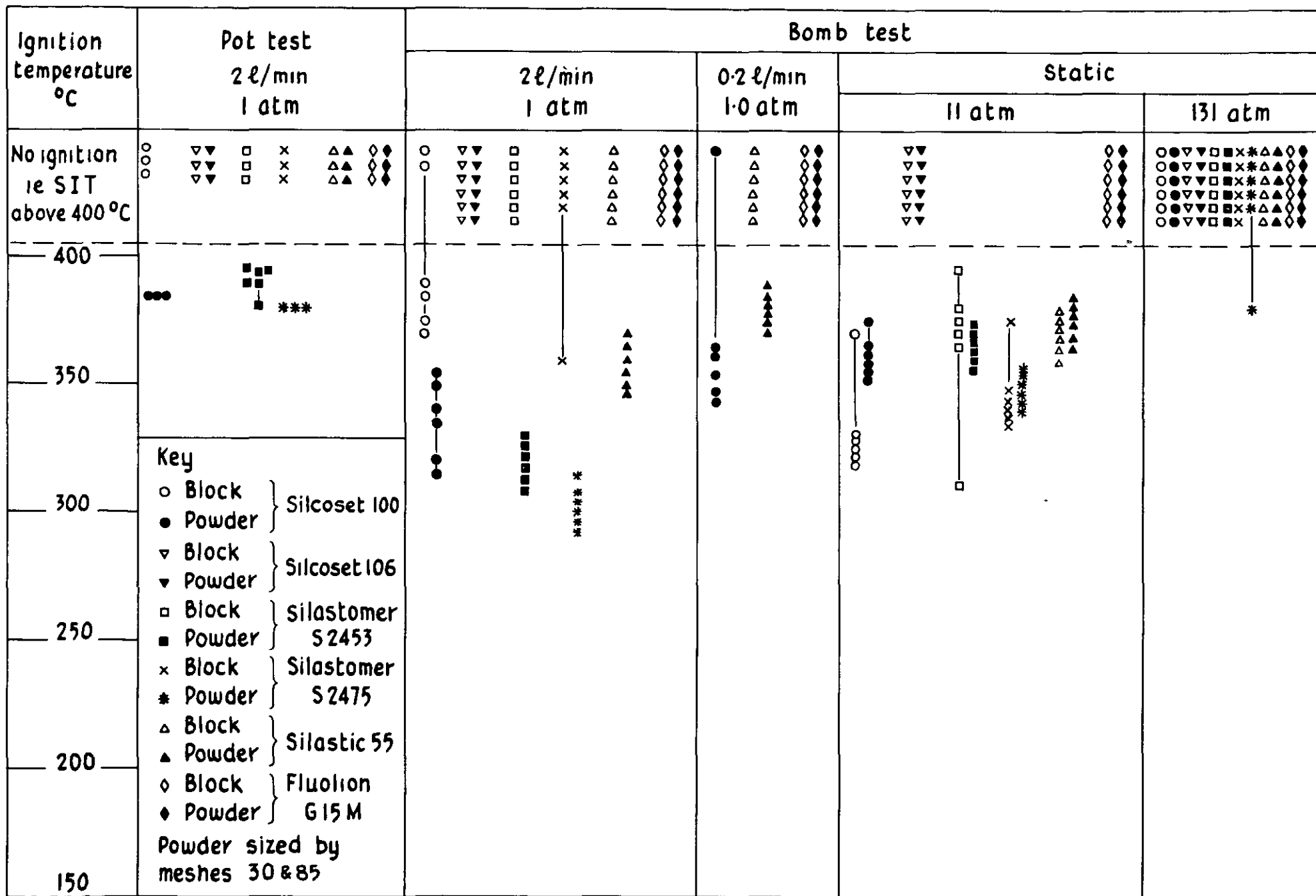
Fig.5 Spontaneous ignition temperatures of elastomers and thermoplastic materials in oxygen

Ignition temperature °C	Pot test 2 ℓ/min 1 atm	Bomb test			
		2 ℓ/min 1 atm	0·2 ℓ/min 1 atm	Static 11 atm	Static 131 atm

Chart plotting ignition temperature data points using symbols for each material.

No ignition ie SIT above 400°C:
- Pot test 2ℓ/min 1 atm: □▽× (repeated rows)
- Bomb test 2ℓ/min 1 atm: □▽× rows, △◇
- Bomb test 0·2ℓ/min 1 atm: □▽ rows, △◇
- Static 11 atm: □ × rows
- Static 131 atm: □▽× rows

Temperature scale: 400, 350, 300, 250, 200, 150

Key

- o Rocol MA-1
- □ Rocol dry film lubricant
- ▽ Silicone grease X-G 315 (MS 33)
- × Sealing compound ZX-32 (DAG 517)
- △ Silicone adhesive MS 2705
- ◇ Loktite D

Fig 6 Spontaneous ignition temperatures of lubricants, sealing compounds and adhesives in oxygen

Material	"Pot" temperature °C														
	220	230	330	340	345	350	360	365	370	375	380	385	390	395	400
Nylon 66 (new) Block												xxx	ooo		
Powder															xxx
Silcoset 100 Block										xxx		xxx			xxx
Powder								xxx			xx ooo				
Silcoset 106 Block									xxx		xxx		xxx		xxx
Powder									xxx		xxx		xxx		xxx
Silastomer S2475 Block							x				x				xxx
Powder			xxx			xxx	xxx	xxx	ooo						
Silastomer S2453 Block							xxx				xxx		xxx		xxx
Powder										xxx	oxxx	xxx	xxoo	ooo	
Silastic 55 Block												xxx	xxx	xxx	xxx
Powder										xxx		xxx			xxx
Fluolion Block										xxx		xxx			xxx
Powder										xxx		xxx			xxx
Rocol-dry-film lubricant									xxx		xxx		xxx		xxx
X-G 315									xxx		xxx		xxx		xxx
Z X 32															xxx
M S 2705			xxx		xooo	ooo									
Loktite D	xxoo														

Key
x ≡ no ignition   Chronological order of tests is
o ≡ ignition   from left to right

Fig.7 Details of 'pot' tests

DETACHABLE ABSTRACT CARD

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ON THE SPONTANEOUS IGNITION TEMPERATURE OF ORGANIC MATERIALS IN OXYGEN

Doubts have been expressed on the significance of the current 'Bomb' and 'Pot' tests used to measure the spontaneous ignition temperature of organic materials in high and low pressure oxygen   An investigation by the British Oxygen Company to explore some of these doubts and to test new materials is described and the results are discussed. Suggestions are made for improved 'Bomb' and 'Pot' test procedures, and for investigations into the basic nature of ignition processes and the relationship between laboratory tests and field conditions.