Evolution of a High Temperature Sealing Material Technology

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Introduction

The two main functions of a sealing material are to provide an impermeable barrier through and across which the retained medium cannot penetrate and, where appropriate, to ensure maintenance of the load imposed by the bolts onto the seal so that there is sufficient surface pressure on the gasket for continued sealing.

The latter requirement means that the sealing material must not react under service conditions in any way that allows excessive loss of bolt extension. The former requirement implies that the sealing material will not be modified by the service conditions so that the initial impermeability is lost.

These requirements therefore limit the functionality of a sealing material and point to a traditional weakness, the binder system present. The binder system in sealing materials has traditionally been an elastomer irrespective of which of the traditional manufacturing methods, “it” calendering or a variant of the paper route, was used. When used in service conditions that do not lead to excessive creep or stress relaxation as a result of the presence of thgre polymer or alteration or loss of that elastomer then there was no shortcoming as a result of the use of that elastomer. However, only modest temperatures and many media are required to remove the elastomer from the sealing material with enhanced leakage, at least, resulting. Thus the presence of elastomer in the traditionally required quantities is a very real Achilles heel.

Avoiding the Achilles heel

In the move to non-asbestos based sealing materials, the shortcomings of creep, stress relaxation or the removal of binder and other material have become even more important as the non-asbestos fibres themselves are either organic or have a poor reinforcing capability or both. As a result of this, the non-asbestos materials made by the two traditional manufacturing routes have had their service temperature limits and service conditions reduced in light of field, rather than laboratory, experience.

In an attempt to compensate for these shortcomings the formulators of these materials have reduced the levels of the elastomers and the permeability of the resulting materials has increased as a result. However, the end user can control this by, as many do, asking for ROTT test reports from TTRL, or other independent organisations, in order to assure themselves that room temperature tightness has not been sacrificed in order to minimise the shortcomings caused by the presence of the elastomer binder.

The shortcomings introduced by the use of a binder system that was unstable within the intended functional temperature range led to materials made by alternative routes come to the fore. Materials such as high tech elastomers, with or without diluent fillers, PTFE sheet materials and, above all, exfoliated graphite, have captured a significant proportion of the remaining market although the traditional materials continue to be sold in huge volumes for successful use within their limited temperature capability.

The high tech elastomers are particularly suited to automotive application where the material cost is offset by the manufacturing methods they allow and the consequential very high efficiency material utilisation but they find little industrial application. The industrial market is now dominated by exfoliated graphite and PTFE.

The polymer PTFE is famous for chemical resistance but has been infamous in industrial sealing, on the basis of earlier generations of PTFE based sheet sealing materials, for excessive bolt load loss. This excessive loss of bolt extension resulted in leaks and, in the limit, very potentially hazardous gasket blow out enhanced by the low coefficient of friction of the material. These failures were not as a consequence of loss of the polymer as such failures were recorded at service temperatures far below the 380 °C limit beyond which PTFE begins to decompose at a very low rate and is thus lost from the seal but were due to creep. This problem has been overcome by modern PTFE sheet materials such as Sigma, a biaxially orientated PTFE based sheet. Such materials have properties that allow the safe use of PTFE as a sealing material up to 260 °C with media at up to pressures of 85 Bar. But beyond this temperature the binder, the PTFE, again becomes an Achilles heel.

As indicated above, a material made with no elastomer or polymer content of any type, exfoliated graphite sheet, has takeover a vast amount of the market that would traditionally have been served by asbestos based materials with an elastomer binder. This material has superb sealing properties and it amenable for use in a very wide range of gasket styles. It consists of a soft flake material that has been chemically opened in to “books” which intermesh to form the familiar sheet material.

This material however, apart from chemical resistance limitations, has it’s own, quite different, Achilles heel in that it is subject to oxidation. This oxidation, even when the material is in the purest form, limits the operational temperature. It has also been recognised that the probability of a failure of exfoliated graphite due to oxidation is a function of many factors but there are three main ones factors; the service life, the service temperature, the gasket style and that the high thermal conductivity exacerbates the problem. Many of the failures due to oxidation have been as a result of a progressive inwards removal of graphite that was initiated by the oxygen present in the atmosphere.

Consequently, for a service life of about five years the service lives of various gasket styles incorporating exfoliated graphite to a value of about 320 °C to 350 °C for sheet service, see References 1, 2 & 3, about 450 °C for spiral wound gaskets and about 550 °C for Flexpro covered serrated metal core gaskets.

The TTRL report referenced above provides the following upper service temperature limits for various periods of service for graphite sheet gaskets:

		Required Service Life [Years]			
		10	5	3	I
Upper Service Temperature	[°C]	305	320	330	370
Upper Service Temperature	[°F]	580	610	630	690

Forms that are less pure and consequentially include traces of oxidation initiators as impurities have lower service limits whilst forms with additions of oxidation inhibitors only temporarily delay the inevitable oxidation. Over time scales such as given above oxidation inhibition systems have no significant beneficial effect.

There is therefore a need for a material with minimal elastomer content that has good chemical resistance and if not subject to oxidation.

Previous Attempts to Provide a Solution

There have been mica based materials available for many years which may be considered, falsely, to provide the required solution because of the well known thermal and chemical properties of mica. However, these also fall in to the elastomer trap. Such materials are made by one or other variant of the paper making route. Due to the nature of mica in that it is impossible to exfoliate in the way that graphite exfoliates, the packing of the mica plates together, even when there are no other materials present, results in a foraminous structure. The interconnected voids of that structure produce leakage paths unless there is sufficient elastomer present to fill those voids. If sufficient elastomer is present to do that then the stress retention characteristics suffer.

There is therefore still an elastomer based Achilles heel with these materials that is illustrated by the test data shown below :

Test Data for Typical Commercially Available Mica Sheet Sealing Material

Thickness	mm	1.96	1.95	2.10	2.01	1.54	1.41
ASTM F36 Compression	%	10.8	8.5	18.7	10.0	14.3	17.1
ASTM F36 Recovery	%	69	70	42	79	40	35
BS 7531 Stress Retention [300°C & 40 MPa]	MPa		1.4			30.2	26.4
DIN 52913 Stress Retention [300°C & 50 MPa]	MPa	4.1		25.7	6.8	37.1	
DIN 3754 Gas Permeability	mL/min	⊗	⊗	∅	1.9	4.8	∅

Where ⊗ indicates that the result was less than 0.1 mL/min
and ∅ indicates that the result was greater than 20 mL/min

The materials from which the data in columns 1, 2 and 3 was obtained have very low or marginally acceptable permeabilities but only at the expense of very poor stress retention properties such that service failures are highly probable. The materials from which the data of columns 3, 5 and 6 was obtained have good or acceptable stress retention but at the expense of permeability, in two cases too high to measure. The laboratory data indicates that these materials do not provide a viable material. That conclusion is verified by service experience where in the sheet form they are only recommended by the suppliers for very low pressures and where they are found to be totally unsatisfactory for use as the filler of a spiral wound gasket.

An Alternative Binder System

Over the last few years work has been progressing on an alternative which overcomes to a great extent the problem with the use of existing binder systems. This work revolves around the use of vermiculite in chemically exfoliated form [CEV]. Vermiculite is a common mineral widely used that is a member of the mica family but unlike all other members of the family it is capable of being exfoliated due to it being chemically modified in the ground over eons of time. CEV is derived from the common mineral vermiculite by a chemical means that results in a dispersion of very thin, typically less than 250 nm, and highly flexible plates which have the very useful property of acting as an inorganic binder whilst leaving the bound composite flexible. This means that this material can take over the binding function of the elastomer of sealing materials.

The material CEV also provides other benefits. Being a member of the mica family CEV is totally unaffected by the oxidation effects that plague graphite. It can be used as a sealing material to about 1100 °C, service is well proven at 970 °C. It also has extremely good chemical resistance and can thus be used in sealing applications where, apart from the 260 °C temperature resistance, PTFE would have been used. Furthermore, and in total contrast to graphite, like other members of the mica family, it has good electrical and thermal insulation properties that are useful in gasketing applications.

In the following the development paths and properties of sealing materials for sheet gasket, Flexpro serrated core gasket facing and spiral wound gasket filling applications are discussed.

Sheet Sealing Materials bound by Chemically Exfoliated Vermiculite

As the result of the work carried it is possible to make sheet sealing materials in the range 0.8 mm to 4.5 mm thick in sheet sizes at least 1.6 m wide and a length of 1.6 m or above. This material is a blend of two types of vermiculite with a small proportion of an elastomer binder. The second form of vermiculite, apart from the CEV, is thermally exfoliated vermiculite, TEV, which is commonly used as a potting compost addition, in plaster, in fire resistant coatings and as a packaging material.

The binder, present as a processing aid as much as anything, can be any suitable elastomer, nitrile is generally used, at a level of about one third of that present in “it” calendered sheet sealing materials. The sheet material is supplied on a metal reinforcement with the current form being on tanged 0.1mm 316 stainless steel and is therefore free of adhesive. The table below gives an overview of the properties of this material, by traditional sheet gasket test methods, as a function of thickness:

Recent Routine Production Thermiculite 815 Quality Assurance Test Results

Nominal Thickness	(mm)	1.0	1.5	2.0	3.0
Actual Thickness	(mm)	1.11	1.60	1.86	2.93
Bulk Density	(g/cm^3)	1.98	1.72	1.58	1.19
Facing Density	(g/cm^3)	1.11	1.26	1.19	1.18
ASTM Compressibility	(%)	42.6	40.0	43.9	48.7
ASTM Recovery	(%)	16.1	8.1	6.8	6.3
BS Stress Retention	(MPa)	38.7	31.9	29.4	22.3
DIN Gas Permeability	(mL/min)	0.82	0.31	0.05	0.01

These results show the benefit of the CEV binder as, firstly, without the use of such material it would not even be possible to produce these materials unless excessive amounts of elastomer binder were used. Secondly, the use of the CEV requires only an extremely low level of elastomer and this provides a very positive advantage in comparison with traditional elastomer bound sealing materials in terms of the reduction of stress relaxation whilst also providing excellent sealing characteristics.

The results of ROTT testing of this material done at TTRL in Montreal in 1997 according to the Draft 9 procedure contrasted against other sheet materials are summarised below :

	G_b	a	G_S	T_{Pmin}	T_{Pmax}	S_{100}	S_{1000}	S_{3000}	S_{10000}
Thermiculite Sheet	1,906	0.20	456	18	58,645	4,788	7,588	[9,400]	12,026
Aramid	290	0.38	2	1,136	30,448	1,692	4,087	6,225	[9,800]
Glass	1,767	0.22	65	110	30,684	4,867	8,077	10,285	[13,000]
Gla/Ara	2,360	0.19	50	68	29,068	5,661	8,768	10,804	[13,000]

Aramid - aramid fibre reinforced calendered sheet material
Glass - glass fibre reinforced calendered sheet material
Gla/Ara - glass and aramid fibre blend reinforced calendered sheet material

Note : G_b , G_S , S_{100} , S_{1000} , S_{3000} , S_{10000} all have units of lbf/in^2

[ ] Values interpolated from ROTT graph

Corrosion and Salt Water Service Benefits

A feature of vermiculite over graphite that was mentioned above is that it is electrically insulating. This adds an advantage in that it means that in some circumstances the corrosion that would have been produced by graphite is avoided.

To investigate the relative corrosion initiation characteristics of exfoliated graphite sheet and Thermiculite sheet some corrosion testing was conducted by AEA Technology's National Centre for Tribology in the UK, Reference 4. The testing was carried out in accordance with the ISO

9227:1990 standard over a period of 600 hours in a salt spray mist. Samples of exfoliated graphite sealing material sheet and Thermiculite sealing material sheet, both on tanged 316 stainless steel cores, were tested in contact with plain carbon steel and 316 stainless steel. As a control, samples of Sigma biaxially orientated PTFE sheet sealing material were also included in the testing. In order to simulate service conditions more closely it was arranged for the test gasket samples to be under a surface stress of 40 MPa on assembly.

At the end of the tests there was corrosion visible on the 316 stainless steel surfaces that had been in contact with the graphite but none was visible on the surfaces that had been in contact with the vermiculite sheet material or with the PTFE based material.

The immediate relevance of this testing to North Sea and other off shore applications is that sheet graphite gaskets are known to cause corrosion unless exotic alloys are used for the flanges.

Halogen and Sulphur Content Benefits

A further feature over graphite and the formerly used asbestos sheet is that the sulphur content of the Thermiculite materials is extremely low. There are no sulphur or sulphur including compounds added to cure the elastomer or contaminating the vermiculite raw. This is particularly important to processes such as Pressurised Water Reactors for power generation.

Graphite, except in the exceptional form where the manufacturing process is not based upon the use of suphuric acid, always contains a significant amount of sulphur. This has led to concern by end users over the possibility of suphur induced metallurgical problems especially from imported forms of graphite sheet.

Thermiculite in all current forms has a very low water extractable halogen content. Halogen compounds are present in one form or another as contaminants in most forms of sealing materials. They were often present in asbestos and were at particularly high levels in some deposits of asbestos as a result of which there were implicated in the initiation of corrosion in service.

The content of halogen containing materials is zero or very low in Thermiculite. The results of an analysis of Thermiculite 815 by a US test house are given below:

Water leachable chloride ion:	24 ppm
Water leachable fluoride ion:	36 ppm
Water leachable SO_4 as S:	33 ppm
Total Sulphur content:	120 ppm
Total Halogen content:	1815 ppm

Note that the last two results, total Sulphur content and total Halogen content, were based upon analysis methods that measure the total content by liberating it in a very high temperature burning treatment of the material. As a result, material that would not be liberated at service temperatures shows up in the analysis. This fact has been reinforced by further testing in Europe where, as expected from the mineralogy of vermiculite, the tightly bound crystal lattice Fluorine present as a result of substitution during the formation of the mineral, has been shown not to be liberated at temperatures relevant to PWR operation.

Thermal Conductivity Benefit

For some applications in Fuel Cells and Automotive Exhausts the thermal conductivity of gasket materials is an issue. As expected the thermal conductivity of graphite is high but as vermiculite is a thermal insulator that for Thermiculite sheet is low. Reference 5 details some measurement done in the UK the results of which are summarised as that the value of the thermal conductivity of 3 mm Thermiculite 815 sheet is less than 0.2 W m^{-1} K^{-1} at room temperature.

Flat Core Forms of Sheet

As with any new product and process, the process of improvement continues and the possibilities for further development emerge as process experience and component bounds have been explored.

One area that has been investigated is the use of flat cores rather than the tanged core. The obvious disadvantage is the need for and adhesive but if phenolic based systems are used and professionally applied then the disadvantages from the over use of a thermoplastic adhesive that gave the original adhesively bonded graphite sheets a bad reputation are avoided. Also, only the minimum amount of organic material is added to the sheet by this route and thus stress loss problems at temperature are minimised. The use of a flat core also allows the manufacture of thinner gauges of sheet material.

Results for two gauges of adhesively bonded SS 316 core are given below

Substrate	0.1 mm Adhesive Coated Steel				
Nominal Thickness	(mm)	0.8	1.5	2.0	3.0
Actual Thickness	(mm)	0.74	1.61	2.15	3.07
Bulk Density	(g/cm^3)	2.32	1.49	1.26	1.16
Facing Density	(g/cm^3)	1.39	1.04	0.95	0.94
Compressibility	(%)	27.6	42.3	49.9	54.9
Recovery	(%)	23.0	7.6	10.3	7.5
Stress Retention	(MPa)	36.5	30.1	26.8	17.9
Gas Leakage	(mL/min)	0.04	0.03	0.01	0.01

Substrate:-	0.05 mm Adhesive Coated Steel				
Nominal Thickness	(mm)	0.8	1.5	2.0	3.0
Actual Thickness	(mm)	0.74	1.61	2.15	3.07
Bulk Density	(g/cm^3)	1.89	1.07	0.99	0.95
Facing Density	(g/cm^3)	1.45	0.89	0.86	0.86
Compressibility	(%)	27.7	49.5	54.1	55.7
Recovery	(%)	14.8	5.1	6.6	6.1
Stress Retention	(MPa)	36.5	30.1	26.8	17.9
Gas Leakage	(mL/min)	0.31.	0.04	0.08	0.05

It can be seen that, using the route developed to produce an adhesively bonded Thermiculite sheet material, the stress retention has remained high and only suffered a reduction relative to the tanged SS 316 reinforced material for 3 mm thick material. For this gauge the shear on the interface will be at a maximum.

Spiral Wound Gasket Filler

There are very many instances of graphite filled spiral wound gaskets failing in service due to oxidation. It is also well documented, Reference 6, that this oxidation is often initiated at the outside of the sealing element and works inwards to create the failure. There is therefore a real need for a totally oxidation resistant filler material.

The previously available mica filler materials do not provide the required solution as, on their own they do not form a reliable seal, and the inner and outer wraps either side of graphite filled wraps in a sealing element they only provide a temporary solution due to the permeability of the mica filler.

The most difficult part so far of the evolution of the Thermiculite high temperature sealing material has been the development of the required filler foil for spiral wound gaskets. However, this has now been done and Thermiculite spiral wound gaskets are very successfully in service at many sites around the world.

The ROTT test data for the Thermiculite spiral wound gasket generated in accordance with Draft 10 is given below:

	G_b	a	G_S	T_{Pmin}	T_{Pmax}	S_{100}	S_{1000}	S_{3000}	S_{10000}
Thermiculite sheet	1,906	0.20	456	18	58,645	4,788	7,588	[9,400]	12,026
Thermiculite spiral	2,120	0.19	49	42	79,395	5,083	7,868	9,691	12,178

Note : G_b , G_S , S_{100} , S_{1000} , S_{3000} , S_{10000} all have units of lbf/in^2

Some very high temperature Thermiculite spiral sealing tests have been carried out in Europe with results that are very encouraging. The tests were done with internal heating of DN80 PN100 raised face flanges with an assembly stress of 70 MPa. Leakage rate results were obtained with helium as the gas at pressures of 4 Bar and 20 Bar after heating periods of 170 hours. The results are given below :

With helium pressure of 4 Bar : Leakage rate 7 10^{-2} Pa m^{-3} s^{-1} m^{-1}
T2 – 3 Class

With helium pressure of 20 Bar : Leakage rate 3 10^{-1} Pa m^{-3} s^{-1} m^{-1}
T2 Class

As for the sheet material, as the process and formulations of the filler material are further refined then even better results will be obtained.

Flexpro Serrated Metal Core Gaskets

It may be felt that graphite will not be subjected to oxidative attack when used as the facing of a serrated metal core gasket because the very high stress at the first tip of the serrations encountered by any potentially oxidising media would protects all the facing from attack. This is a very valid reasoning but the fact remains that there are many instances of graphite faced serrated metal core gaskets failing in service. Some of these are without doubt due to thermal movement allowing entry by oxygen.

The Thermiculite technology allows serrated metal core gaskets to be covered either with a Thermiculite paste, therefore achieving very high efficiency in the material usage, or by the Thermiculite spiral foil. As for graphite, facings can either be cut from the spiral filler foil whilst it is in the original sheet form or the foil can be slit to the required width and then corrugated to form a tape which can be used to face the required core. Either way a facing with not more than one join in the facing results.

Thermiculite faced Flexpro gaskets have been in service for periods of years in arduous service where graphite faced serrated metal cored gaskets had repeatedly failed. The Thermiculite Flexpro is now a solution of choice selected by the Flexitallic Application Engineering teams in many instances.

Conclusions

An inorganic binder system capable of elimination of the limitations of existing materials has been successfully used during the development of a family of high temperature sealing materials.

When used in each of the gasket styles discussed, these materials outlined above are giving good service in a wide range of arduous applications.

The development work continues and some not yet revealed will result in the Thermiculite technology penetrating further areas of the sealing market.

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