

## Rubber – Steel Interface Failure in Pipeline

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### Introduction

Rubber bonding to a variety of metals, particularly steel, plays an important role in the design and manufacture of equipment for the mining and chemical industries all over the world. It allows the strength and stiffness of steel to be combined with the wear, and corrosion and chemical resistance of rubbers. It also allows thick and flexible liners to be built that are resistant to extreme slurry wear, thermal stress etc. Some examples of this use are tanks, pumps, impeller liners or pipeline spools. Figure 1 is an example of lined pipeline spools similar to those discussed in this presentation.



Figure 1. Pipeline spools

The technology of bonding rubber to steel has been developing for many years but industry is still confronted with unexpected and expensive failures caused by unusual service conditions or strange behavior of materials in some environments. Unfortunately, these failed parts are frequently discarded or sent for rebuilding without a more in depth evaluation of the cause.

### Objective

The objective of this presentation is to create awareness in scientific and technical societies about certain issues in bonding rubber to steel that may lead to premature interface and rubber failure.

### Pipeline Failure

These types of problems seemed to be detected during the investigation of the failure of a pipeline over 10 km long in a North American plant. The pipeline, which is 200 mm in diameter, was constructed from 12.5 meter long spools lined inside with 6 mm thick natural rubber compound. The materials and process used in pipeline manufacturing could be accepted as industrial standards. An infrared inspection of the pipeline conducted by the plant after 5 years of service at a temperature of approximately 50°C showed a significant temperature increase in numerous areas of the pipe surface (figure 2) which was likely related to liner failure. Furthermore, inspection of the individual spools revealed a large number of blisters, rubber breakdown, and adhesion failure between the rubber and steel (figure 3). A segment of spool with characteristic blisters was sent to Polymer Engineering Company Ltd. for further laboratory evaluation.

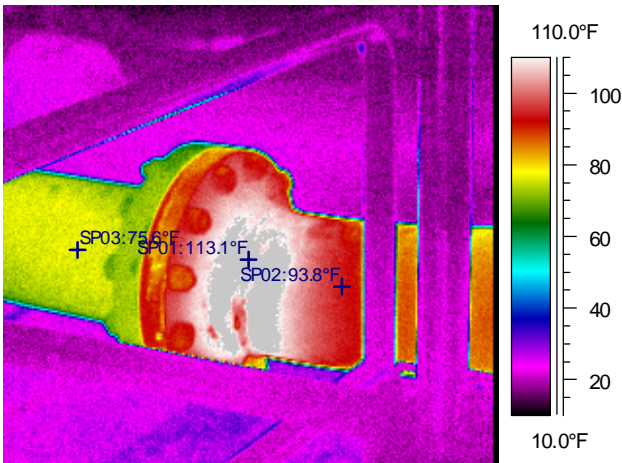


Figure 2. Thermographic picture of spool



Figure 3. Liner failure

### Laboratory Evaluation

The laboratory evaluation of the segment of failed spool included: (1) analysis of blister water, (2) pipeline water chemistry (3) rubber analysis (4) microscopy of rubber-steel interface and EDX evaluation of materials (5) reaction of components of the adhesive system with water (6) rubber water absorption, mechanical properties, and hardness.

Major contaminants of the blister water and pipeline slurry are shown in table 1 together with the analysis of the blister water and extract (in boiling water) from rubber A compound which is similar to that used in the liner.

Table 1. Blister water analysis

Ion	Concentration mg/c		
	Blister water	Rubber A	Pipeline slurry
Calcium	17	4.6	440-500
Copper	<0.1	<0.1	NA
Iron	492	<0.1	NA
Manganese	250	<0.01	NA
Potassium	26	2.1	20-30
Sodium	41	8.5	160-210
Zinc	38	0.9	NA
Magnesium	9	0.4	1020-1150
Chloride	827	0.6	90-140
Bromide	500	ND	NA
Sulphate	78	2	5000-5500
Acetates/Formates	500*	6	NA
pH	4	6	7.3-7.6

\*approximation based on acetate

NA – not tested

ND – below detection limit

The concentrations of iron, manganese, chlorides, bromides, and organic acids in the blister water were much higher than the concentration of these ions in pipeline slurry. Also, the pH in the blister water was acidic, contrary to the neutral slurry pH. The extract from the rubber was also almost neutral with relatively low levels of iron, manganese, chloride, bromide ions, and organic acids.

Further elementary analysis of rubber and water from the extraction of rubber compound A, similar to that used for the liner, is shown in table 2.

Table 2. Elementary analysis of rubbers

Elements	Concentration ppm		
	Failed rubber Surface	Steel interface	Rubber A
Calcium	234	78	62
Iron	129	200	61
Manganese	8	316	1.3
Potassium	492	372	216
Sodium	34	276	662
Chlorine	870	690	100
Bromine	NA	NA	ND

NA – not tested  
ND – below detection limit

The data presented indicates that it was very unlikely that the major blister water contaminants such as iron, manganese, chloride, and bromide ions came from the rubber or slurry and were probably in some way related to the rubber-steel interface.

It should be mentioned that some iron and manganese ions are powerful catalysts of rubber degradation. High concentrations of iron and manganese, likely in ionic form, near the rubber-steel interface were also accompanied by the presence of acetic and formic acids, not only in the blister water but also in the rubber, with the highest concentration near the interface. This was confirmed by GC MS analysis of the gaseous components of the rubber released at an elevated temperature (see table 3). It is expected that these organic acids could have been created as rubber oxidation by-products in a reaction catalyzed by metal ions.

Table 3. Acetic and formic acids as gaseous components released from liner rubber

Compound	Ret. time min	Concentration µg/g	
		Surface	Interface
Acetic acid	9.14 – 9.23	102	1392
Formic acid	9.86 – 9.96	80	1845

Failed rubber mechanical properties were also evaluated (table 4)

Table 4. Mechanical properties of failed rubber liner

Properties	Testing Method	Units	Value
Tensile strength	ASTM D412	MPa	0.82 (0.06)
Elongation at break	ASTM D412	%	160 (20)
Hardness	ASTM D40	Shore A	36

The data presented in table 4 also indicated very low tensile strength and elongation at break of the failed rubber, which confirms the advanced aging process in rubber and explains the easy disintegration of the liner under the stress created by the blisters and slurry movement. As mentioned earlier, it is suspected that some ions created in the corrosion process, such as iron and manganese, migrated into the liner and accelerated rubber aging.

Optical microscopy of the rubber-steel interface is shown in figures 4, 5, 6, and 7. Specimens were specially prepared to obtain an intense blue colour in the rubber. The excess of hydrated iron oxides from the surface were also removed from some samples by selective etching.

**Figures 4-7.**  
**Microscopic pictures of rubber steel interface cross-section (4) and interface surface (5-7)**



Figure 4



Figure 5

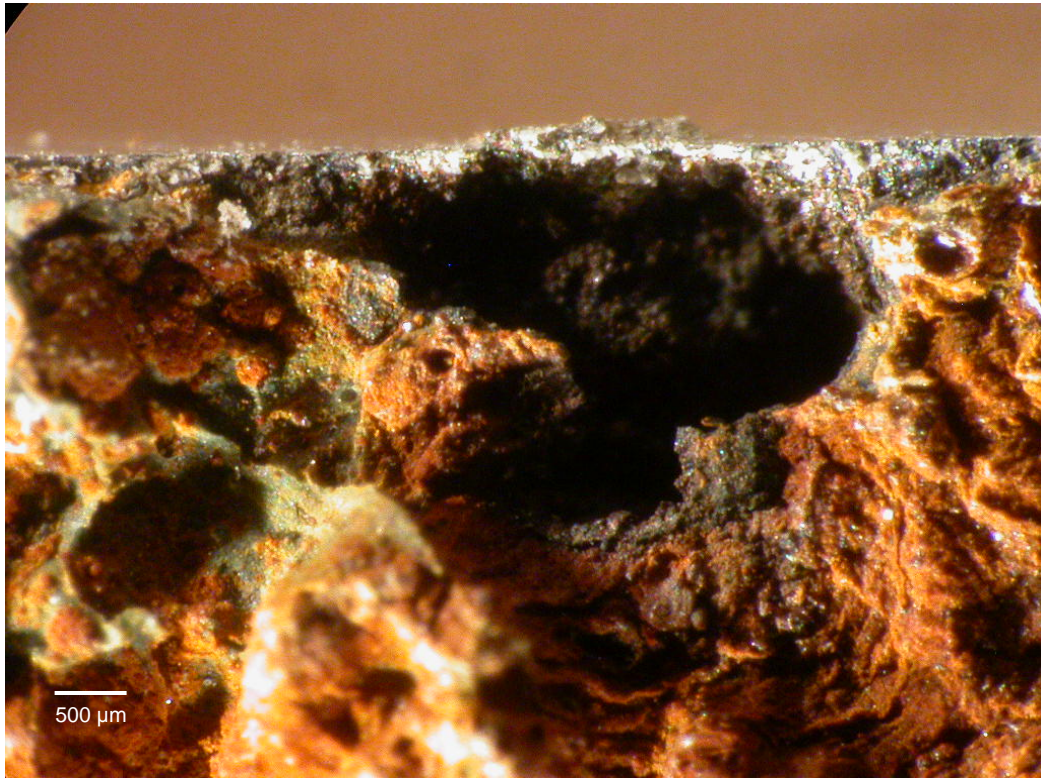


Figure 6.

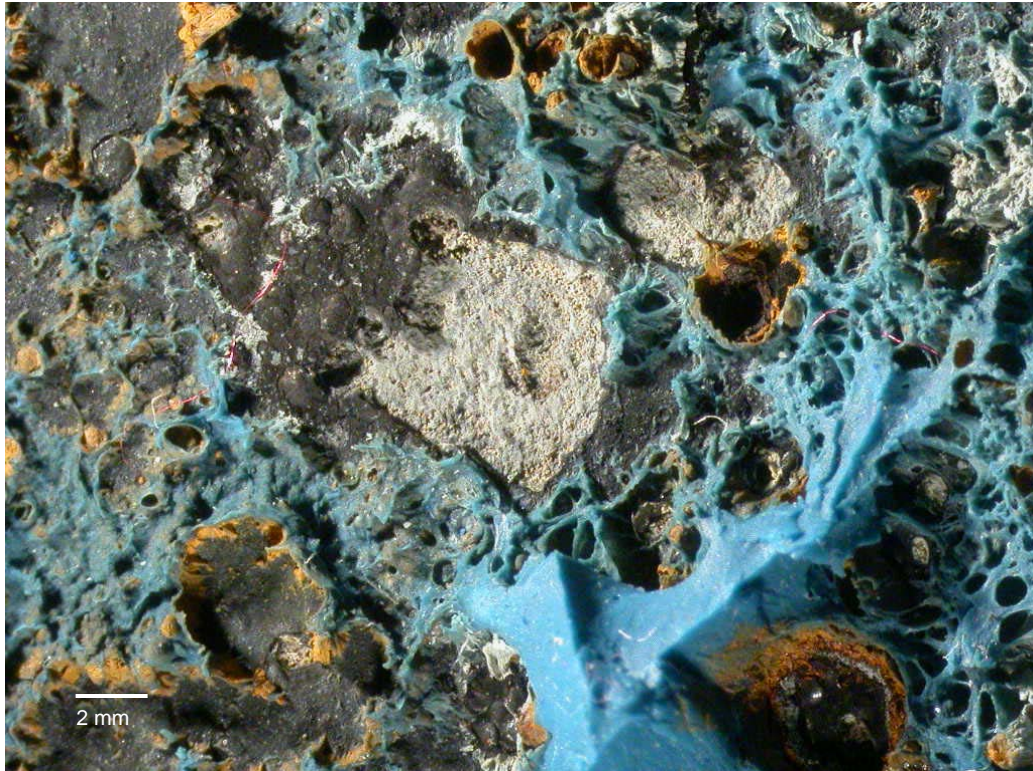


Figure 7

The optical microscopy revealed that the rubber in the vicinity of the interface showed significant porosity with a spongy appearance in many places that were in contact with the adhesive layer. Voids in the foamy structure were filled with a brownish substance – likely precipitated iron oxides. There were many small pinholes and signs of blisters in the adhesives layer with eroded metal cavities underneath that are likely associated with corrosion. In particular, the cross-section visible in figure 4 shows that some regions of the steel/rubber interface are full of microfoam-like cavities in the rubber. Some of the cavities are filled with porous brownish iron oxide deposits. A significant portion of the adhesive system film seems to be intact except for some damage caused by corrosion where the primer is lifted from the steel and the cavity was eroded beneath by the electrochemical corrosion process. The iron extracted from the steel seems to be transferred by diffusion to the rubber and rubber cavities, and some further precipitated in the form of oxides.

Another look at the surface of the steel/rubber interface is shown in figure 5. The blue rubber remains and black adhesive surfaces are visible with some exposed gray or rusty metal surface. Failure of the interface occurred approximately 50% within the rubber, and 30% between the adhesive and rubber. Also, some failure is seen between the metal and adhesive layer in the examined area. In the centre, a blister and entry to a large cavity in the steel is visible with some rusty steel exposed where the protective coating is missing, likely in a cathodic disbondment process known in coatings. It could be expected that the blister was initiated by a coating defect.

An electron microscopy image of the rubber-steel interface is shown in figure 8 with EDX analysis of material layers presented in table 5.

Electron microscopy, including EDX analysis, indicated the presence of large quantities of chlorine in the primer and adhesive. Titanium was present only in the primer as identified on the SEM images and the presence of bromide was characteristic only to the adhesive used.

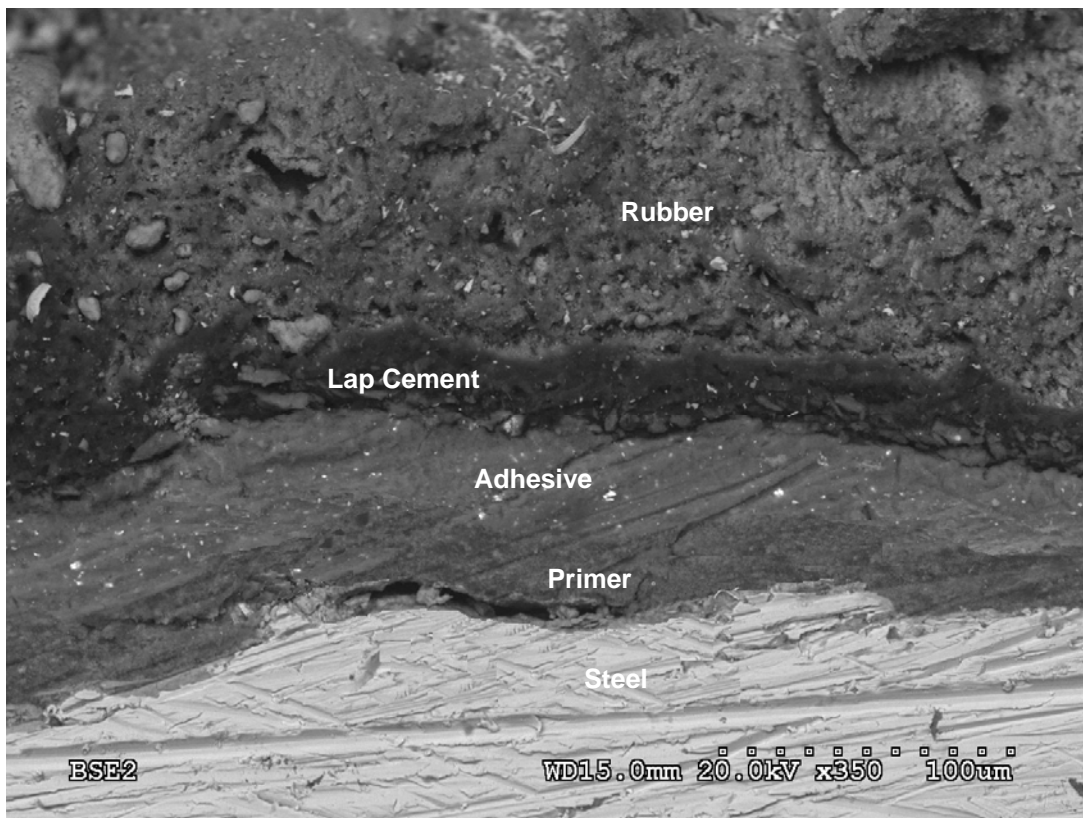


Figure 8. SEM image of steel-rubber interface

Table 5. EDX analysis of material layers in the steel-rubber interface

Elements	Concentration %				
	Steel	Primer	Adhesive	Lap cement	Rubber
Carbon	10.2	45	60.2	82.0	80.1
Oxygen	ND	21	6.8	10.3	12.9
Sulphur	ND	0.3	1.0	0.9	0.9
Chlorine	ND	<b>10.0</b>	<b>20.9</b>	0.8	ND
Titanium	ND	10.7	0.2	ND	0.5
Iron	89	7.8	7.2	5.8	2.2
Bromine	ND	NA	<b>3.1</b>	ND	ND
Manganese	0.7	NA	ND	ND	ND

The difference in the density of material layers allowed different components of the interface to be distinguished and thickness to be estimated. The thickness of all coatings was found to be according to industry standard and close to the manufacturers recommendation. EDX examination also showed the presence of manganese in the steel, which was likely the source of manganese ions in the blister water.

Furthermore, table 6 shows contaminants in water after boiling of fresh dried and cured samples of the adhesive, and primer films most likely used in manufacturing of the discussed pipeline.

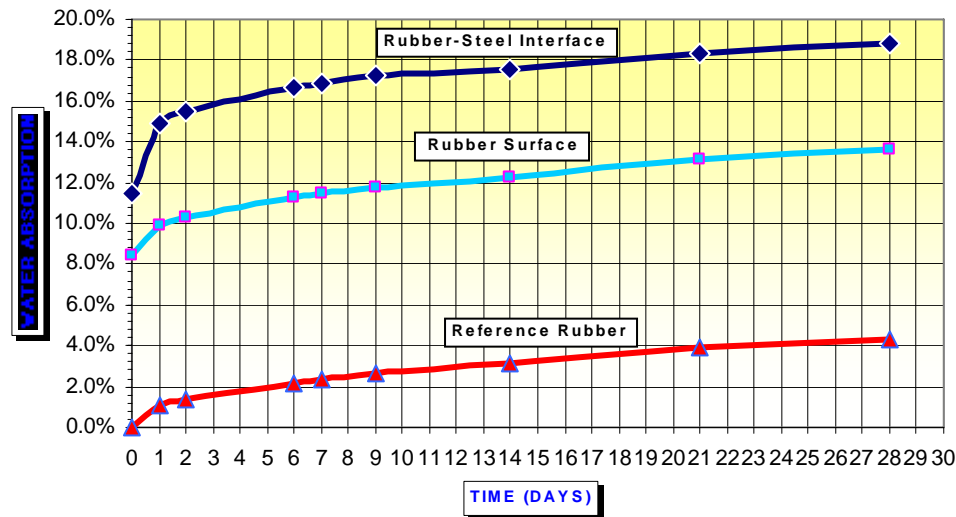
Table 6. Water contaminants from boiling of adhesive and primer films

Elements	Concentration mg/l	
	Primer	Adhesive
Calcium	2.5	7.4
Copper	<0.1	<0.1
Iron	<0.1	0.8
Manganese	<0.01	0.02
Potassium	2.1	1.8
Sodium	17	112
Magnesium	<0.2	16
Chloride	202	1159
Bromide	1	532
Organic acids	3	3
pH	5.5	2.0

Results indicated that the adhesive used in manufacturing of the failed pipeline was likely the main source of the hydrochloric and hydrobromic acids. Corrosive acids were likely created during the service conditions due to contact of warm water with some adhesive components.

To identify the source of the water needed for adhesive hydrolysis and electrochemical processes associated with corrosion, the rubber liner was tested for water absorption at 23°C according to ASTM D471 as shown in figure 9.

Figure 9. Water absorption of failed liner rubber

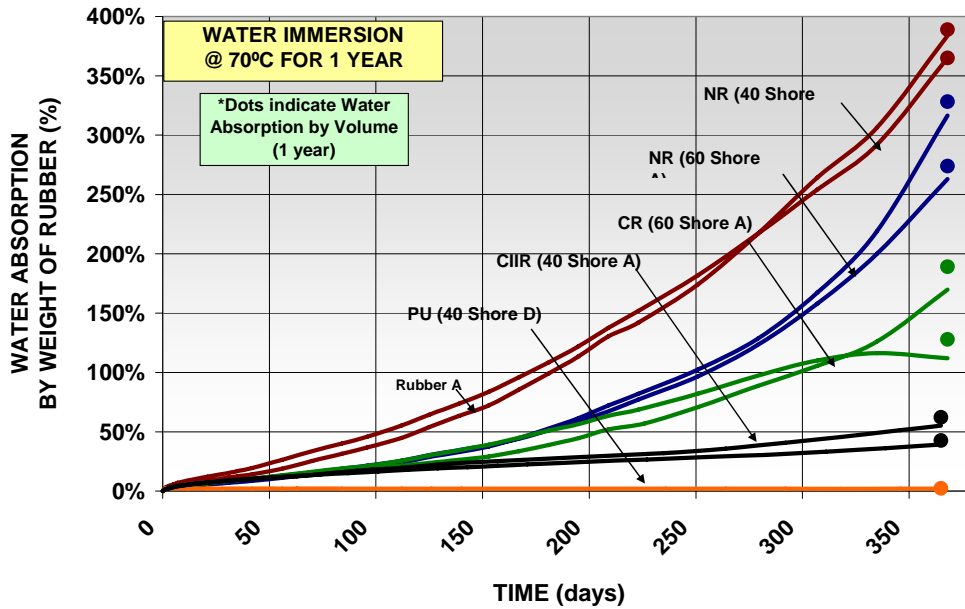


It has to be noted that the failed rubber liner had relatively high initial water absorption of approximately 12% near the interface and 8% near the surface several weeks after removal of the spool from service. After immersion in water at 23°C, water absorption of the samples increased rapidly during the first day of immersion (to approximately 15% for the interface and 10% for the surface specimens). From this point, both samples followed the water absorption of the natural rubber reference sample. After 30 days of immersion, the interface specimens absorbed almost 20% water.

To find out whether the high water absorption observed is a phenomenon related only to the examined liner, or whether it is a general trend in rubber materials, further testing was done. Water absorption of the rubber used for manufacturing of the discussed liner was also compared to other rubber compounds designed for industrial liners, including different grades of natural rubbers, neoprene, chlorobutyl rubber and polyurethane. Rubbers were exposed to water at 70°C following the procedure of ASTM D471 for a period of up to one year to accelerate the process (figure 10).

The results clearly indicated that, at certain service conditions, rubbers may absorb very significant quantities of water reaching almost 400% by weight. The water absorption rate seems to increase with exposure time and exposure temperature. These rubber properties should be taken under serious consideration when an adhesive system is designed for an application with possible prolonged contact with water. This water absorption, in combination with the so called "cold wall effect" which may occur at some service conditions will also cause liquid water condensation and accumulation near the steel rubber surface which may lead to accelerated corrosion and bond failure. This issue seems to not always be addressed during development of adhesive systems, material testing procedures, or material selection.

Figure 10. Water absorption of selected rubbers



## Conclusions

1. The majority of rubbers used for bonding with metals frequently showed very high water absorption in prolonged contact with water, particularly if this contact occurred at elevated temperatures.
2. Water absorbed by rubber may directly affect the rubber-metal interface or may undergo condensation in the vicinity of the metal interface due to the “cold wall effect” particularly when voids are present.
3. A significant quantity of water, which may be present in the rubber bonded with metal, could accelerate metal corrosion directly or indirectly.
4. Some adhesives may react with water in the metal-rubber interface and corrosive compounds may be created, including hydrochloric and hydrobromic acids. This may be an issue when elevated service temperatures are expected.
5. Steel corrosion products may migrate into the rubber and accelerate rubber aging, particularly during elevated temperatures in service. This process is suspected to generate formic and acetic acids.
6. Most of the standard testing procedures for evaluation of bonding rubbers to metal do not take into consideration long term water absorption by rubbers.
7. Further work on environmentally friendly and user friendly rubber to steel adhesives is required, particularly when elevated temperature service is expected in an aggressive environment.

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