RIGID POLYMERIC FOAM BOARDSTOCK TECHNICAL ASSESSMENT

Dan Schroer, Michelle Hudack, Mark Soderquist, and Inken Beulich
The Dow Chemical Company, Midland, MI (U.S.A.)

Abstract

Phenolic foam insulation is commercially available in Europe and Asia. Recently, a study was conducted that assessed the performance of European and Asian sourced phenolic foam versus North American extruded polystyrene (XPS), and polyisocyanurate (PIR) insulation products.

This paper discusses the performance aspects of phenolic foam insulation relative to both polyisocyanurate (PIR) and extruded polystyrene (XPS) foam. The findings are summarized and discussed herein:

Introduction

A variety of rigid polymer foam insulation boardstock materials are available commercially. In North America, two of these competitive materials are Extruded Polystyrene (XPS) or Rigid Polyurethane Foam (PUR). Polyisocyanurate (PIR) is a special class of PUR that exhibits enhanced fire resistance.

Phenolic foam is another class of rigid insulation boardstock. Phenolic foam insulation was manufactured and sold into the North American market in the 1980's and early 90's, mainly as roofing insulation. Claimed benefits were high insulation value and excellent fire resistance. High moisture absorption potential and residual acid present in the foam allegedly resulted in significant corrosion issues. Class action lawsuits were filed against corporations in the early 1990's. Past litigation in North America focused on corrosion allegedly caused by phenolic foam used in metal deck roofing applications. The resultant roofing failures and subsequent litigation are still fresh in the minds of the building community. This will most likely pose a barrier to widespread phenolic foam use as insulation boardstock in North America in the foreseeable future. Today, phenolic foam wall and roofing insulation is no longer produced in the United States or Canada. However, phenolic foam insulation has been re-introduced into Europe and Asia for roofing and walls.

In addition, phenolic manufacturers in Europe or Asia give very specific installation instructions meant to mitigate the risk of similar issues, addressing potential failure modes that still exist when phenolic foam is used with diverse substrates (e.g. metal, concrete, masonry). These instructions include the use of stainless or chrome plated fasteners, use of vapor permeable moisture barrier sheets, and specific statement not to use the product in areas where it will be exposed to large quantities of water, moisture, or water vapor. There are, however, inherent risks in implementing these highly prescriptive installation techniques at the jobsite.

The recent reemergence of phenolic foam products motivated the authors to undertake a technical assessment to better understand the differences and similarities to other rigid insulation foam boardstock in today's market.

Commercial phenolic foam insulation is made from a resole resin in the presence of an acid catalyst, blowing agents and surfactants. The resole resin is synthesized via a base catalyzed reaction of phenol and formaldehyde in a 1:2 ratio where there is a twofold excess of formaldehyde in the reaction mixture.[1] The phenol and formaldehyde can form addition products such as methyolphenol. The addition products can go on to react with more formaldehyde or they can also react with themselves to form condensation products. The resole resin can then be cross-linked to form the basis of the phenolic polymeric foam structure via temperature (130 - 200°C) or in the presence of an acid catalyst such as toluene or xylene sulfonic acid[1,2]

The phenolic foaming process involves a mixture of the resole resin, acid catalyst, blowing agents such as hydrofluorocarbons, pentane or hexane and surfactants. Closed cell foams need to be cured at temperatures below 100°C or under pressure to avoid vaporization of water which will increase pressure within the foam and cause cells to rupture.

XPS and PIR foam are produced using manufacturing process that have been previously reviewed[3,4].

Experimental

Materials

Two phenolic foam products were evaluated. The first, phenolic foam A is a commercially available product sourced from Asia. Phenolic foam B is a commercially available product sourced from Europe. For comparison, two foam insulation products from North America were assessed. The first is a leading Polyisocyanurate (PIR) foam board sold into commercial and residential sheathing applications. The second is an leading extruded polystyrene (XPS) foam board used in commercial and residential sheathing applications.

The phenolic and PIR foam had facers attached for all physical property testing. The XPS foam evaluated is not produced or sold with a facer. The facer descriptions are listed below in Table 1.

The data gathered for the phenolic foam samples is an average of three thicknesses. At each of these three thicknesses, three samples were measured for a total of nine samples. The PIR and XPS foams were both 25 mm (1 inch) in thickness, with three samples measured for each. The thickness of foam tested is shown in Table 2 below.

Table 1. Sample Facer Description

Foam Type	Facer Information
Phenolic Foam A	Polyester nonwoven fabric
Phenolic Foam B	Composite foil
PIR	Plain aluminum
XPS	None

Table 2. Sample Thickness Description

Foam Type	Measured Thickness
Phenolic Foam A	20, 30, 66 mm
Phenolic Foam B	23, 40, 71mm
PIR	25 mm
XPS	25 mm

Table 3. Summary of Physical Property Methods

Test Procedure	Test Method
Density	ASTM C303-07
Thermal Conductivity	ASTM C518
Compressive Strength	ASTM D1621 Proc A
Dimensional Stability	ASTM D2126
Water Absorption	ASTM C209-07
Water Vapor Transmission	ASTM E96
pH	ASTM C871 (modified)
Cell Size	In house Microscopy

Test Results

Group comparisons[5], such as shown in Figures 1 are an output of the statistical software JMP®. The foam type is listed on the x-axis. Individual results are shown as black dots on the y-axis. The top and bottom points of the diamond represent the 95% confidence interval for the mean of the data set. The horizontal line through left and right points of the diamond represents the mean of the data set.

Density:

Density has an impact on a number of physical properties, specifically those associated with the mechanical properties of the foam such as compressive strength. As density increases, the strength generally increases as well. The measured core density (facers removed), is shown below in Figure 1 with units of pounds per cubic foot. Only the phenolic B sample was measured to have significantly higher density than the other three samples.

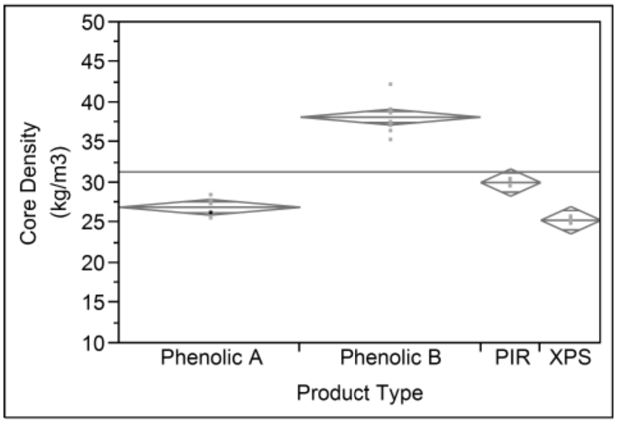

Figure 1. Core Density, ASTM C303-07

Thermal conductivity:

Thermal conductivity measurements were conducted in accordance with the ASTM C1289 heat aged method, via ASTM C518. The foams were heat aged for 90 days at 140 degrees Fahrenheit prior to being measured. This method is commonly utilized for PIR foam products. Both phenolic foam samples exhibited lower thermal conductivity (higher R-value) relative to the PIR or XPS samples.

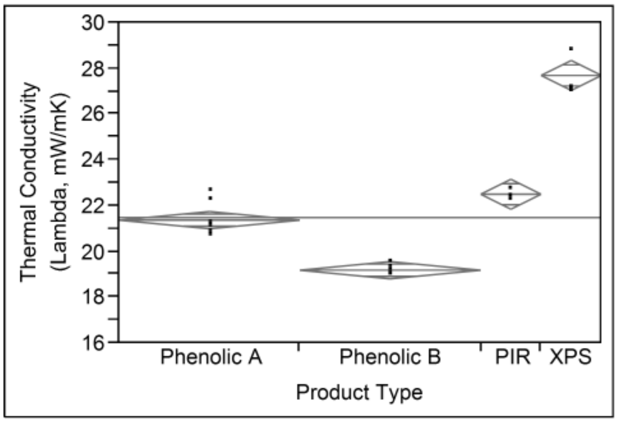

Figure 2. Thermal Conductivity, 90 Day Heat aged @140F, ASTM C518

Compressive Strength:

Despite differences in density, little significant difference was observed in the compressive strength of the four samples. All four samples are suitable for use as rigid insulated foam sheathing.

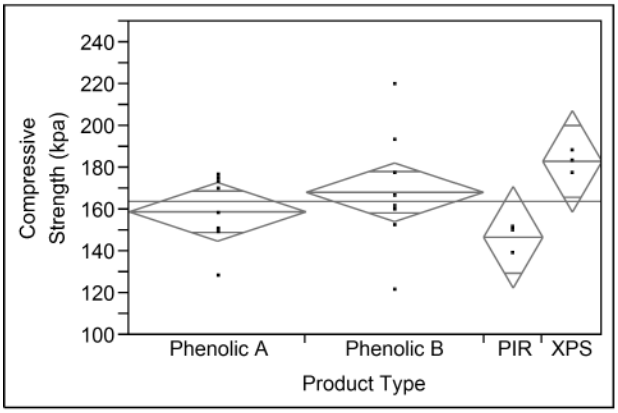

Figure 3. Compressive Strength, ASTM D1621 Procedure A

Water absorption:

Initially, the four foam samples were measured according to ASTM C209, specified in ASTM C1289, which is a 2 hour soak time. A significant difference in water absorption level was observed for the phenolic foam samples relative to PIR or XPS.

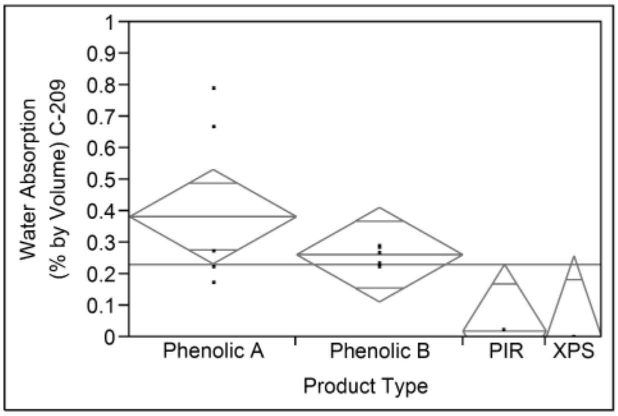

Figure 4. Water Absorption (% by Volume) ASTM C209 – 2 hour soak

Resulting from the 2 hour water absorption data, a longer term water absorption study was conducted. The foam samples were submerged as in ASTM C209, but measured over a 90 day period. All tests were conducted with facers attached. Sample size was 300mm x 300mm (length and width) for all samples. Thickness of foam measured in the water absorption study is shown in Table 4.

The samples were measured initially and then after submersion for 7 days, at which time the thermal conductivity was also measured. The samples were then submerged a total of 30 days at which time they were measured for water absorption and thermal conductivity and so on.

As shown in Figure 5, the water absorption of the phenolic foam samples increased dramatically in the 90 day period relative to the PIR or XPS samples.

The water absorbed by the foam samples over the 90 day test period had a detrimental impact on thermal conductivity. After 7 days of submersion, both phenolic samples had lost enough thermal resistance to perform inferior to both PIR and XPS foams. As the duration of the test continued, phenolic Foam A dropped to 50% of the original measured thermal resistance performance. Phenolic Foam B dropped to 35% of the original performance. Comparatively, the XPS maintained 97% over the same period, and the PIR sample maintained 82% of its original performance.

Table 4. Water Absorption Sample Thickness Description

Foam Type	Measured Thickness for water absorption study
Phenolic Foam A	20 mm
Phenolic Foam B	23 mm
PIR	25 mm
XPS	25 mm

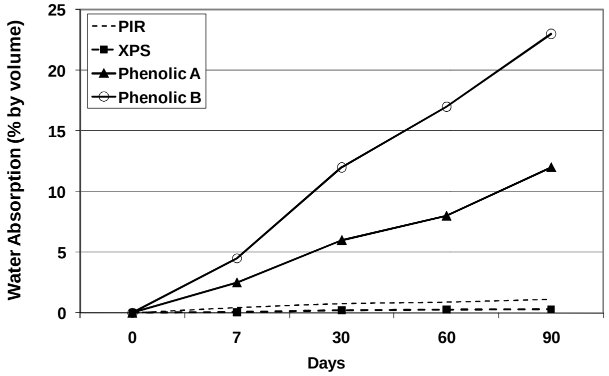

Figure 5. Water Absorption Results, 90 day soak, ASTM C209-07 (extended)

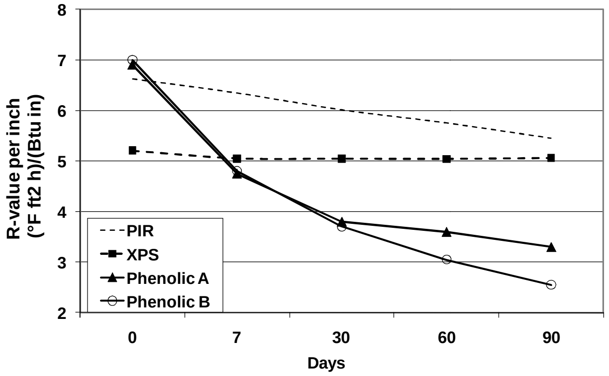

Figure 6. Resulting R-Value/Inch after water soak, ASTM C518

Thermal dimensional stability:

Dimensional stability was measured according to ASTM D2126, following the 158 Fahrenheit, 97% Relative Humidity condition listed in ASTM C1289.

Although the phenolic foam samples had slightly improved performance relative to the PIR and XPS samples in the thickness direction, the difference is not believed to be significant in application use. Not shown, but no significant performance difference was observed between the four foam samples in the length (extrusion) direction, with the four samples ranging between -0.5% to 0.5%

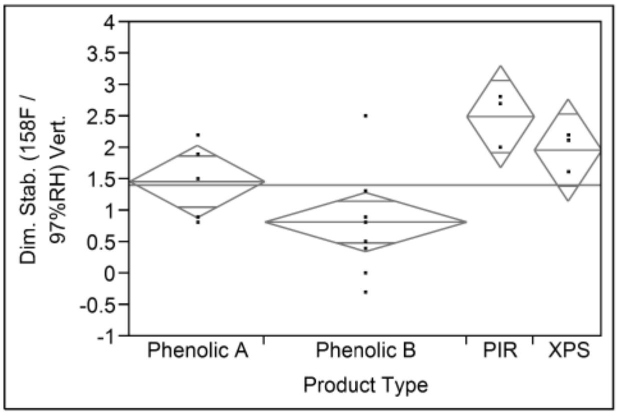

Figure 7. Dimensional Stability, Thickness Direction, ASTM D2126

Water Vapor Permeability:

Water vapor transmission (WVT) levels varied across the foam samples, with the PIR foam having no measureable WVT due to the presence of aluminum facers on the samples. It is expected that the phenolic and XPS foam samples would achieve similar performance if a similar facer was used. However, the phenolic foam and XPS samples used other facer designs or no facer at all, which resulted in the performance shown in Figure 8. This WVT performance would need to be taken into consideration when designed a building thermal envelope to prevent attainment of unwanted dew points. (1 perm-in = 1.459e-12 kg/Pa-m-s)

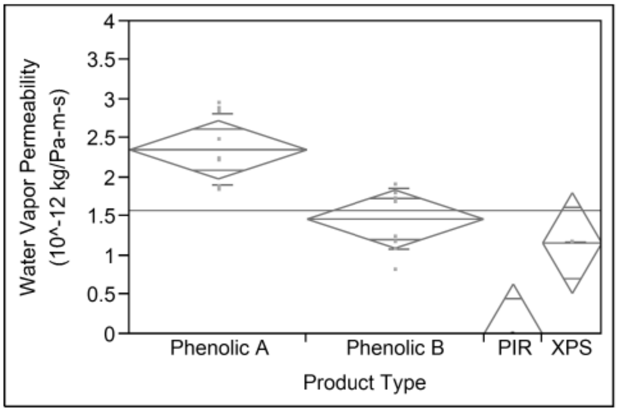

Figure 8. Water Vapor Permeability ASTM E96

Cell Size:

Both phenolic foam samples measured smaller cell size than the XPS or ISO foam. Small cell size improves thermal resistance by reducing the radiative component of foam thermal conductivity[6].

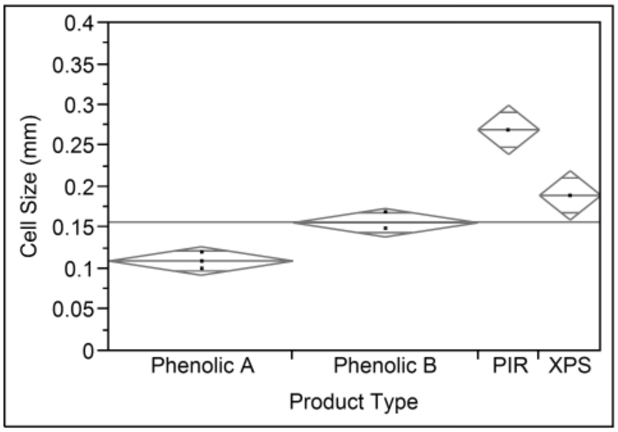

Figure 9. Cell Size, Internal Test Method

Corrosion:

The propensity for phenolic foam to induce corrosion has been a historical issue with phenolic foam sheathing and roofing boards in North America. As mentioned earlier, in the 1980's and early 1990's, litigation was taken against phenolic foam manufacturers in the United States due to corrosion of metal roof decking upon which the foam was placed for insulation. This resulted in product being withdrawn from the market

A pH environment less than 4.0 can lead to corrosion of iron and steel at accelerated rates.[7,8,9] For pH values less than 4.0, ferrous oxide is soluble. The oxide dissolves as it is formed rather than depositing on the metal surface to form a film. In the absence of this protective film, the metal is in direct contact with the acid solution and corrosion proceeds at accelerated rates.

The results of two pH tests are shown in Table 5. The column labeled "ASTM 871 Test" displays the results of the full pH test method, during which 15g of core foam is ground in a stainless blender with 400 mL of DI water until milkshake consistency. (The blending portion of the method typically takes less than 60 seconds.) This suspension is then boiled in a glass beaker for 30 minutes. The resultant filtrate is drained through a paper filter and measured for pH. However, typical service conditions of foam insulation do not see such elevated temperature, such as the 30 minute boil stage. Hence, the method was modified. The column labeled "pH, Modified ASTM 871" follows the same method, but eliminates the step of boiling the solution. The two phenolic foams measured a pH of 3.6 and 2.1 respectively, versus 5.4 and 7.5 for PIR and XPS when using the modified method. The phenolic samples evaluated in the modified test result in a solution with a pH less than 4.0. This could raise concern regarding potential corrosion issues when these products are used in contact with iron and steel.

Table 5. pH Results, ASTM 871

	pH, ASTM 871 Test	pH, Modified ASTM 871
Phenolic A	2.7	3.6
Phenolic B	2.0	2.1
PIR	3.8	5.4
XPS		7.5

Fire and smoke:

Phenolic foam is well known to have excellent fire and smoke resistant properties.[10] Limited in-house fire testing was conducted to compare the relative fire performance of these foams. An internal test method, referred to as Mobil 45 was conducted on the foam samples. The test setup is shown in Figure 10. A brief description is as follows: a 216 mm x 51mm x 13mm sample is mounted at a 45 degree angle from horizontal. A natural gas burner with an inner flame cone of 1.5" is then placed under the sample. The flame is held under the sample until no more visual degradation of the foam is observed. The flame propagation and smoke level are visually evaluated, and mass loss is measured on the sample following the test. Visually, the flame propagation was similar between the phenolic and PIR foams, however the smoke level was observed to be noticeably less with the phenolic foam samples. The XPS foam is not suitable for this test method and was not evaluated.

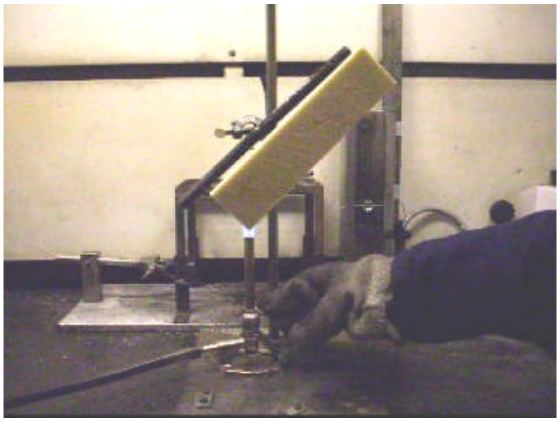

Figure 10. In-House Fire Test

Table 6 displays the resultant mass lost after the fire testing was completed. Mass loss was comparable between the 3 sample types.

Table 6. Mass Loss, Mobil 45 fire test

	% Mass Loss
PIR	**5%**
Phenolic A	**5%**
Phenolic B	**5%**

Formaldehyde:

Liquid chromatography (LC) was used to determine the amount of unreacted formaldehyde monomer remaining in the phenolic foam samples. The total residual formaldehyde found in both phenolic foam samples ranged from 137 – 264 ppm. (Table 7)

As a comparison, the raw materials used to produce PIR and XPS foam do not measure a reportable level of formaldehyde.

Table 7. Residual Formaldehyde in phenolic foam samples

Sample	Residual Formaldehyde (ppm)
Phenolic Foam A, 20mm	253
Phenolic Foam A, 30mm	225
Phenolic Foam A, 66mm	137
Phenolic Foam B, 23 mm	207
Phenolic Foam B, 40 mm	264
Phenolic Foam B, 71 mm	177

Blowing Agent:

Gas chromatography Mass Spectrometry (GCMS) was used to analyze the blowing agents that were present in the foam. A syringe was used to withdraw the blowing agents trapped in the cells of the foam. The extracted blowing agents were then analyzed via GCMS. The phenolic A samples contained isopentane, isobutane and n-pentane as blowing agents and the phenolic foam B samples contained chloropropane and isopentane. Both GCMS and pyrolysis gas chromatography measurements were able to identify isopentane and chloropropane blowing agents in the phenolic foam A and B samples respectively.

The PIR foams assessed here were produced with hydrocarbon blowings agents (mixed pentane isomers). The XPS foams were produced using a zero ozone depletion potential formulation[11], utilizing blowing agents such as 1,1,1,3-tetrafuoroethane (134a).

Discussion

Intellectual Property Analysis:

An intellectual property assessment was done for phenolic foam insulation to better understand if the prior issues with phenolic foams such as corrosion and moisture absorption had been addressed. The patent search was conducted in the Chemical Abstracts database. The search strategy was broad and based on phenolic foams and corrosion or water absorption or formaldehyde emission. Patent activity from 1997 – 2008 shows an average of 2-3 patent applications being published per year (Figure 11).

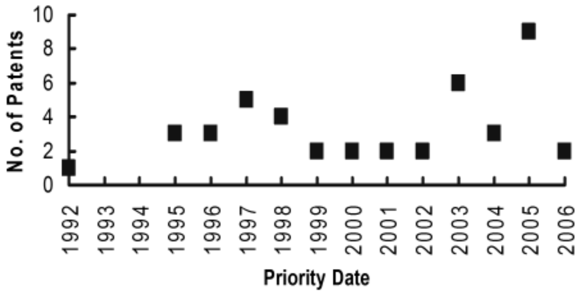

Figure 11. Number of phenolic foam patents over time (priority dates) from Derwent World Patent Index search.

The patent activity around phenolic foam technology covers processes for making phenolic foams, long term stability of the foam with an emphasis on maintaining R over time, corrosion prevention, water absorption and formaldehyde emission. The solution to both corrosion and moisture absorption is the use of additives such of neutralizing agents and inorganic drying agents, respectively. Also, testing of phenolic foam boards show acidic conditions with pH levels of 2.1-3.6. It appears that acidic foam and potential corrosion issues still exist today.

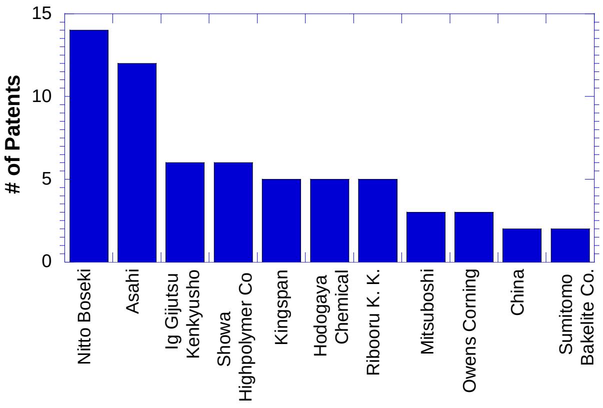

Figure 12. Number of phenolic foam patents versus assignee from Derwent World Patent Index search.

Conclusions

Benefits of phenolic foam insulation:

- High insulation performance
  - High R-value. Measured R/in = 6.7 – 7.5, versus 5.0 – 6.5 for XPS and PIR respectively

    - Small cell size reduces radiative portion of foam thermal conductivity[6]
- Excellent fire performance
    - Low smoke generation and flame spread.

Disadvantages of phenolic foam insulation:

- Water absorption
    - Results in significantly reduced thermal resistance
- Corrosion Potential
    - low pH accelerates corrosion of iron and steel
- Potential EH&S issues
    - - residual formaldehyde present

The phenolic foam evaluated in this study mimics the characteristics of phenolic foam introduced into North America in the 1980's and 1990's. The inherent issues and benefits and phenolic foam appear to still exist today.

References

1. (a) Klempner, D., Sendijarevic, V., (Eds.). (2004). Phenolic Foams by Paul T. Kelly. *Handbook of Polymeric Foam and Foam Technlogy, 2nd Edition*, 447-456. (b) Gordiziella, A.; Pilato, L.A.; Knop, A., (2000). Phenolic Foam. *Phenolic Resins Chemistry, Applications Standardization, Safety and Ecology, 2nd Edition*, 158 – 169

2. Odian, G. (1991) "*Principles of Polymerization, 3rd edition*", p. 127

3. Lee, S. T. (Eds.). (2000). *Foam Extrusion.* Lancaster, PA: Technomic

4. Klempner, D & Frisch, K. C. (1991). *Polymeric Foams*. Munich, Vienna, New York: Hanser pp. 96-131

5. Sall, J., Creighton, L., Lehman, A. (2005), *JMP Start Statistics*, Thomson Brooks/Cole pgs 164-166

6. Chau, V. V., Bunge, F., Duffy, J., Hood, L. (2011). Advances in Thermal Insulation of Extruded Polystyrene Foams, *Cellular Polymers, 30*, 95-113

7. Rossum, J.R., Fundamentals of Metallic Corrosion in Fresh Water. p. 4

8. DOE FUNDAMENTALS HANDBOOK, CHEMISTRY. 1015/1-93. Volume 1 of 2 Ch. 02 pp.15

9. *The Control of Corrosion Under Thermal Insulation and Fireproofing Materials – A systems Approach* NACE International. RP0198-98. pp.21

10. Troitzsch, J., International Plastics Flammability Handbook. Munich, Vienna, NewYork: Hanser pp. 30-32

11. Costeux, S., S. Lee, R. Smith, M. Barger, J. Alcott, D. Beaudoin, H. Clayton, S. Donati, J. Duffy, R. Fox, D. Frankowski, K. Giza, L. Hood, T. Hu, C. Kruse, T. Morgan, C. Shmidt, W. Stobby, C. Vo (2009). *Zero Ozone-Depleting Foaming Agent Technology for Extruded Polystyrene Foam*, FOAMS 2009, Iselin NJ

Acknowledgements

We would like to thank Bill Larson for his expert opinion regarding corrosivity of ferrous metals.