Phenolic resins in refractory applications…
…the story of a material that continues to ‘withstand the heat’

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What are refractory materials?

Refractories are materials based on magnesium oxide (MgO) held together with a binder that are used in furnaces and boilers to process steel, cement, or glass as well as incinerators that operate at high temperatures, typically in excess of 500^0C. Such temperatures are well in excess of that found in the average fire and reflect that needed to withstand contact with molten metals amongst other high temperature applications. In fact, one of the dictionary definitions of the word ‘refractory’ is “stubborn, headstrong or rebellious” indicating that, unlike some foundry applications that are sacrificial, refractories are intended to survive and remain intact through multiple uses. So, the next question to answer is ‘how does a product made using organic binders such as resins or pitch pull off such a trick? The answer is simple – it carbonizes! Therefore, the story of a successful refractory material is one that carbonizes well.

Phenolic Resins – the ‘preferred’ choice?

A variety of binders can be used when refractories are manufactured. In this article, the use of phenolic resin as a binder for refractories is described and compared with other pitch-based options. The 2010 book, ‘Phenolic Resins – a Century of Progress’ by Louis Pilato, he writes that there are several factors supporting the use of phenolic resins in comparison to other refractory binders. These include the following:

1. Both adhesion and green body strength are high.

2. It is a thermosetting resin system whose strength on curing is high, and the size and stability of the resulting refractory components are good.

3. The ratio of fixed carbon is high and maintains high strength on carbonization. Phenolic resins are the preferred binder for carbon containing refractories.

4. The hazardous properties and industrial environmental issues are lower than those associated with the use of pitch binder.

While Louis Pilato is undoubtedly an advocate for phenolic resins in this book, as a prominent Fellow of the Society of Advancement of Material and Process Engineers (SAMPE) he must remain objective in his assessments in order maintain his credibility and enhance his reputation for unbiased assessments. So why does he use the word ‘preferred’ and, if so, ‘preferred to what’? Well, since phenolic resins have only been around for just over a century, there must have been materials in use for the handling of molten metal before that. In fact, in his summary, Pilato ‘gives the game away’ by mentioning explicitly ‘pitch binder’. However, before we go on to consider those alternatives, it is worth saying a word about the applications for which phenolic resins, in both their novolac and resole forms are typically used. The following table summarizes the situation:

	Carbon Brick	Iso-Pressed	Tap-Hole Clays	Monolithic
Novolac Powder	X	X		X
Novolac Liquid	X	X	X	
Novolac (molten)	X			
Resole (water-based)	X	X	X	
Resole (solvent-based)	X	X	X	

Carbon bricks represent the largest single use of refractory binders and is inevitably one of the most competitive for those materials. Iso-pressed technologies are somewhat more niche in their application but allow the continuous pouring of steel, thereby avoiding ingots. Meanwhile, taphole clays are used for sealing iron smelters and typically use liquid systems for the “green” strength that Pilato speaks so positively about. By contrast, monolithic applications are typically based on dry powders which can be vibrated to create large mouldings.

Why did phenolic resins supersede pitch?

Coal tar pitch (CTP) is the residue left after the removal creosote oil or anthracene oil. Historically, it has been a plentiful and relatively inexpensive raw material. However, it does tend to vary in quality depending on source and subsequent processing. Heat treatment has typically been adopted to achieve more consistency, creating the identified product, catchily entitled 'Coal Tar Pitch, Heat Treated' (CTPHT) with CAS number 65996-93-2. Historically, this was typically the pitch binder that acted as the benchmark for other binders and arguably the one which Pilato was referring to in his 2010 comparisons.

From a quick assessment of the structures of the carbonized materials, it is relatively easy to understand why phenolic chemistry provides better adhesion and green strength. In the 1987 book 'Industrial Aromatic Chemistry', Franck and Stadelhofer show how the mesophase for Coal Tar Pitch is slow to develop at 400^{0}C, meaning that there is little or no green strength at that temperature:

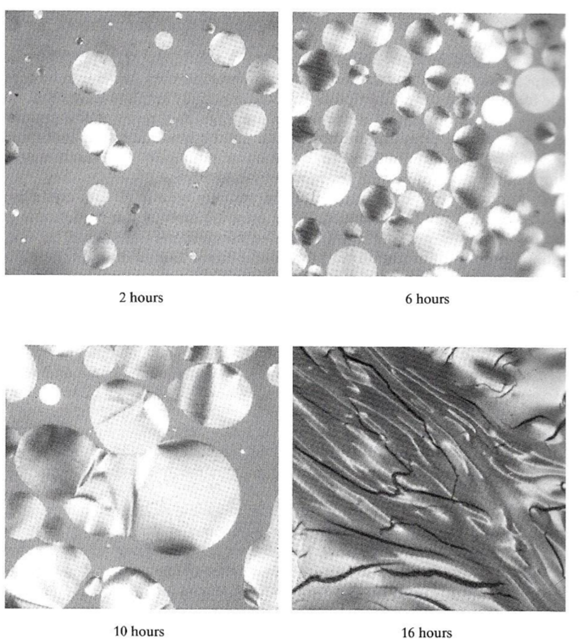
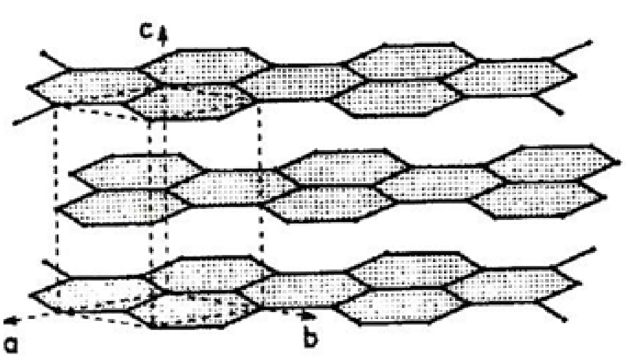


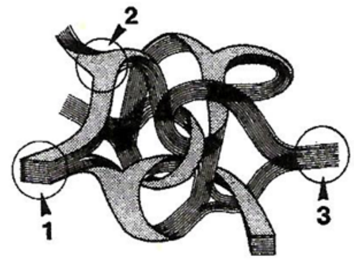
Figure 13.2: Progression of mesophase formation and coalescence during pyrolysis of filtered coal-tar pitch at 400 °C

This carbonization process ultimately results in a highly defined planar structure, very similar to graphite:



This structure tends to provide a lower modulus material which can be argued to be more forgiving in processing terms, but has less green strength and dimensional stability.

By contrast, phenolic resins offer a significantly stronger matrix, based on a three-dimensional cross-linked isotropic structure producing a very hard ceramic-like material, often referred to as glassy carbon.



It is this structure that drives the advantages of high thermal stability, resistance to corrosion and thermal shock plus high hardness/strength. It is therefore little surprise that Pilato was able to characterize this system as 'preferred', even though it might be slightly less forgiving in its processability. While some have argued that CTPHT remains the binder of choice on processing grounds, it is hard to disentangle their rationale from the fact that the cost of Coal Tar Pitch based materials are significantly less expensive than phenolics.

The environmental time-bomb

20 years ago, it was already becoming evident to many that the presence of high levels of (PAHs) polycyclic aromatic hydrocarbons – most notably benzo-α-pyrene – was likely to cause carcinogenicity concerns. Levels of benzo-α-pyrene in CTPHT are typically in the range of 0.5-1% which had caused the heat-treated material to be listed as a Category 1b carcinogen. In more recent times it has been declared under REACH as a Substance of Very High Concern (SVHC) and has a sunset date, after which only authorized uses will be permitted.

In response to this impending development, the coal products industry decided to invest in a more refined version of CPTHT with a further heat treatment step in place. This has been registered by the even catchier name of Coal Tar Pitch High Temperature, Heat Treated (CTPHTHT) under the CAS number 121575-60-8. Commercially, this is marketed as Carbores. This material has lower levels of benzo-α-pyrene at <500ppm (typically around 350ppm) but this is still above the threshold of 50ppm which would be the level required for the material not to be listed as a Carcinogen 1b substance. Therefore, the selection of CTPHTHT as an alternative for CTPHT is seen, at best, as a risk reduction measure rather than a move to a less hazardous solution. Nevertheless, the investment in the manufacture of CTPHTHT in Europe has already reached a capacity of 53,000 tonnes/annum.

Many see this as the promotion of a regrettable substitution, especially bearing in mind that phenolic resins represent a completely legitimate and proven alternative. Indeed, CTPHTHT now appears in the latest version of the influential SIN List (Substitute it Now) updated periodically by Chemsec. It therefore seems that CTPHTHT may have a relatively short shelf-life as an alternative. This is underlined by the fact that the substance is currently under review by the Dutch Competent Authority (RIVM) who are conducting a Risk Management Options Analysis (RMOA) on it.

EPRA will continue to promote the availability and suitability of phenolic resins for the applications outlined in this article in order to permit the selection of less hazardous solutions for the industry.