

Experience with Petroleum Enhanced Coal Tar Pitch

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During the 1990's Koppers Industries has dedicated a significant effort to the development of petroleum enhanced coal tar pitch. This effort has included: 1) identification of suitable petroleum enhancers, 2) laboratory testing of candidate petroleum enhanced pitches, 3) commercial testing of pitches developed, and 4) improvements to address initial shortcomings of the early product. This paper will trace the history of this significant product development from its beginning to the improved product today that has more than four years commercial application. Laboratory and commercial data that demonstrate the equal and potentially superior performance of this product for the production of anodes will be presented.

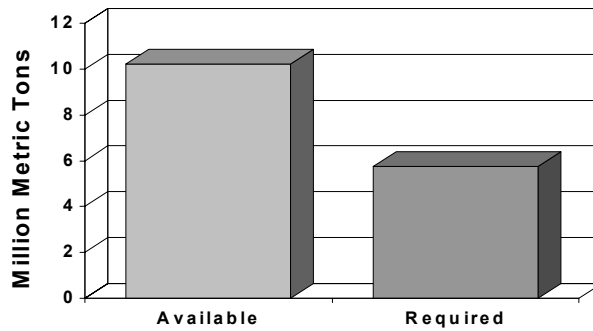
INTRODUCTION

The first coal chemical recovery ovens were installed in the United States in 1893. By 1915, by-product ovens accounted for 97 percent of the metallurgical coke produced in the United States. Since that time coal tar pitch has been the binder of choice for the aluminum, commercial carbon, and graphite industries. In the 1960's more aromatic, higher specific gravity petroleum pitches were developed. Many evaluations of these improved petroleum pitches as binder pitch have been performed with mixed results, but most evaluations have reported uneconomical performance, especially with respect to carbon consumption.^{1, 2, 3, 4}

In the late 1980's and early 1990's the closing of United States coke ovens accelerated due to economic and environmental pressures. As the year 2000 approaches, the closing of United States coke ovens due to environmental regulations has accelerated. These coke oven closings have left coal tar pitch suppliers and users searching for strategies to cope with the shrinking supply of coal tar. These strategies have included: 1) importing coal tar, 2) importing coal tar pitch, 3) developing processes to improve pitch yield and upgrade non-conventional coal tars, and 4) using petroleum streams to supplement the coal tar pitch supply. Each of these strategies has advantages and disadvantages.⁵ The use of petroleum enhanced coal tar pitch will be discussed in this paper.

COAL TAR SUPPLIES

A discussion of coal tar supplies is the traditional "good news/bad news" scenario. The good news is that as Figure 1 indicates the supply of coal tar in the world is more than adequate to produce the pitch needed.



- 10,211 M metric tons crude coke oven tar available worldwide in 1998
- 5,764 M metric tons required to satisfy projected demand

Figure 1 – World Coal Tar Supply

The bad news is that the coal tar is not always located at the point of demand, especially in North America. Figure 2 projects that North American coal tar supplies will decline by 23% between 1997 and 2005.

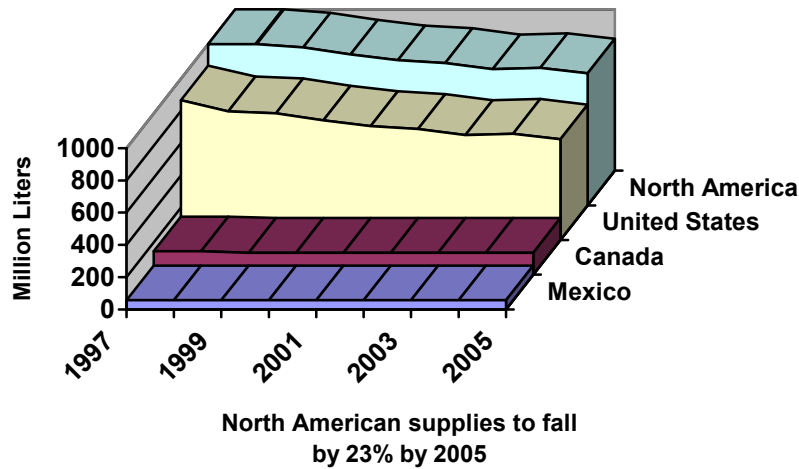


Figure 2 – North American Coal Tar Supply Trends

One could reasonably ask why the shortage of coal tar is concentrated in North America. The answer to that question has two major components. The first and most important component is that North American coking operations have aged and are not competitive with cheaper import coke because of the high maintenance and environmental costs. This non-competitive component has resulted in coke oven closures. The second component is the technological advancements in the steel industry that are affecting coal tar production and coke demand. The introduction of non-recovery coke ovens that do not collect the liquid products produced will result in coke production without coal tar recovery. The development of direct coal injection in the steel production process has resulted in a decreasing demand for coke,

therefore less coal tar production. Also, electric arc furnace steel production continues to grow. This process remelts scrap steel and requires no metallurgical coke.

The next logical question is how severe is the shortage of coal tar. Table I gives North American coal tar pitch demand and coal tar requirements, availability, and deficits for 1995 and 1997 and predictions for 1999, 2001, and 2003.

Table I – North American Binder Pitch Demand

	'000 Metric Tonnes				
	1995	1997	1999	2001	2003
Aluminum Industry	597	666	708	679	701
Commercial Carbon	95	95	95	95	95
Miscellaneous	<u>140</u>	<u>127</u>	<u>118</u>	<u>91</u>	<u>91</u>
Total	<u>832</u>	<u>888</u>	<u>921</u>	<u>865</u>	<u>887</u>
Crude Tar Required	1602	1711	1774	1666	1706
Crude Tar Available	<u>1316</u>	<u>1302</u>	<u>1077</u>	<u>990</u>	<u>929</u>
Tar Deficit	<u>286</u>	<u>409</u>	<u>697</u>	<u>676</u>	<u>777</u>

Predictions indicate the coal tar deficit will increase from 286,000 metric tons in 1995 to 777,000 metric tons in 2003. The tar deficit has the potential to be greater if the amount of idle capacity restarts or new aluminum smelter construction exceeds predictions. One fact seems clear. Strategies to deal with the declining coal tar supply need to be implemented. One of these strategies, the use of petroleum enhanced coal tar pitch, will be discussed in the remainder of this paper.

PETROLEUM ENHANCED COAL TAR PITCH

As has been demonstrated in the previous section, the supply of coal tar for coal tar pitch production is insufficient to produce the pitch necessary for the North American market. Koppers began developing a strategy to deal with this coal tar deficit in the late 1980's/early 1990's. One of the components of that strategy was the development of petroleum enhanced coal tar pitch. This was a bold step because previous attempts to use 100% petroleum pitch as a binder for anodes had resulted in mixed success. It is believed that some of reasons for this mixed success were the lower coking value and total lack of quinoline insolubles in petroleum pitch. Despite the negative experiences with petroleum pitch Koppers began development of a hybrid binder pitch which contained both coal tar and petroleum components. The positive aspects of incorporating petroleum in a binder pitch product are 1) very economical, 2) there are potentially plentiful supplies of suitable petroleum material, and 3) petroleum streams of consistent quality can be obtained. The product development took the approach of building on the positive characteristics of the coal

tar and petroleum components, searching for possible synergies, and developing new processes for combining the two components. The history of the development of this product will be discussed in the following paragraphs.

Two ranges, < 15% Type A and < 40% Type B, of petroleum in coal tar were selected for the initial product development. The effort began with the characterization of approximately seventy-five petroleum derived materials. After characterization and selection of the appropriate petroleum streams, processes for combining the coal tar and petroleum materials were developed. The development began at the bench scale with preparation of candidate pitches followed by production and characterization of laboratory anodes. The results obtained for the laboratory anodes were encouraging and efforts were made to conduct pilot trials of the Type A pitch.^{6,7}

In 1994, a 200 ton batch of Type A pitch was produced on a commercial scale to be used for a pilot anode study. Vibroformed anodes measuring 152 mm x 228 mm x 305 mm were prepared with a control coal tar pitch and the Type A pitch as binder using sized, calcined petroleum coke and butt material. The only discernible difference between the control and Type A anodes was a slight increase in the air reactivity of the Type A anodes.

Also in 1994 a batch of Type B pitch was prepared for a pilot anode study. The higher content of petroleum in the Type B pitch produced a finished binder pitch with lower toluene and quinoline insolubles and a higher sulfur content. Again, vibroformed anodes measuring 152 mm x 228 mm x 305 mm were prepared with a control coal tar pitch and the Type B pitch as binder using sized, calcined petroleum coke and butt material. Results of this study indicated that the binder level for Type B pitch needed to be lower than for the control. Again, the only discernible difference between the control and Type B anodes was a slight increase in the air reactivity of the Type B anodes.

The encouraging results of the pilot scale anode studies led to discussions with several aluminum smelters in an effort to arrange plant trials of the coal tar/petroleum pitch. The first trial conducted in a commercial smelter was a short term trial of Type A pitch. The limited duration trial showed permeability, electrical resistivity, and thermal conductivity advantages for the Type A anodes; but the same disadvantage for air reactivity noted in the pilot anode studies.

The next trial of Type A pitch was a fourteen-month trial conducted at a large smelter. During the fourteen-month period 16,700 tons of Type A pitch were used. The anodes produced were 1200 mm x 594 mm x 800 mm vibroformed anodes with an average weight of 908 kg. A 15 wt. % binder level resulted in a normal green density of 1.59 g/cc for the 115,250 anodes produced with normal baking operations. During this trial there was no observable difference in air burn between the Type A and control anodes. The overall conclusions of the trial were that there was no

significant difference between anode quality or performance when Type A pitch was used as the binder.

Type B pitch has been evaluated in both prebaked and Soderberg operations, although in less extensive testing. The prebaked trial consisted of 520 tons of Type B pitch being used to produce 2,100 anodes weighing approximately 825 kg each. The anode forming conditions were not adjusted for the anode production. The trial anodes gave no significant problems to pot operations, but the average anode density and carbon consumption were slightly inferior for the Type B anodes. It is anticipated that these properties could be improved by optimizing the binder level for Type B pitch.

Approximately 1,000 tons of Type B pitch have been used in a Soderberg aluminum smelter operation. Type B pitch was designed to provide a significant reduction of PAH emissions from the Soderberg operation. The trial Soderberg anodes performed as well as the standard anodes. Emission sampling indicated a significant reduction in PAH emissions.

The results of these commercial trials indicated that an acceptable product had been developed. However, development efforts did not stop. Additional development efforts concentrated on an improved coal tar/petroleum pitch that would give an anode with improved air reactivity characteristics. The objective of improved air reactivity led efforts to reducing the sulfur content of the petroleum component. Through the joint efforts of Koppers and the petroleum material supplier the sulfur content of the petroleum component was reduced by one-half. With this improved coal tar/petroleum pitch successfully developed additional laboratory scale anodes were produced.

The performance of the improved coal tar/petroleum pitch was evaluated by conducting a laboratory anode study. For the study four pitches were selected 1) a 100% coal tar pitch reference, 2) a 85% coal tar/15 % petroleum pitch, 3) a 80% coal tar/20% petroleum pitch, and 4) a 100% petroleum pitch reference. The properties of the four pitches are given in Table II.

Table II –Properties of Pitches Used in the Anode Study

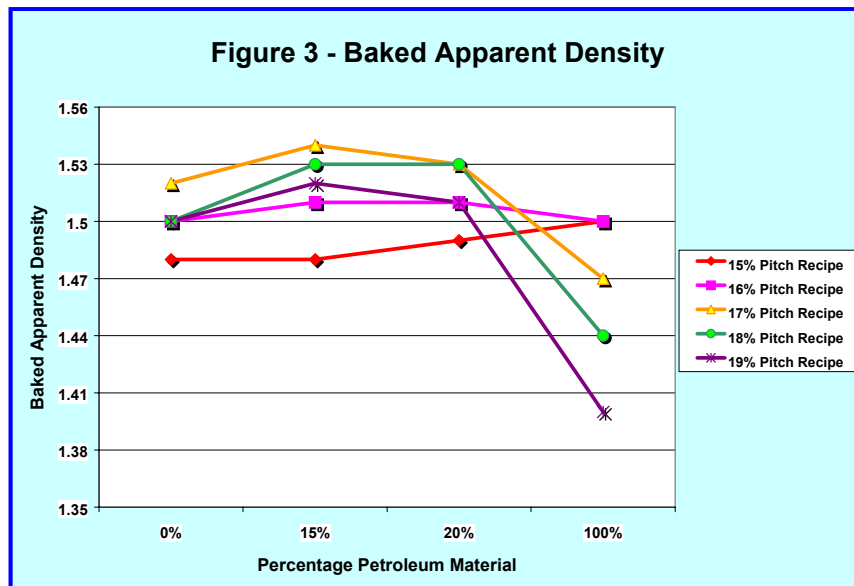
Property	Coal Tar Pitch	15% Petro	20% Petro	Petroleum
Softening Point, °C	109.4	108.5	107.7	108.7
Toluene Insolubles, wt. %	27.5	25.8	24.8	3.5
Quinoline Insolubles, wt%	13.1	12.6	12.6	0
Beta Resins, wt. %	14.4	13.2	12.2	3.5
Coking Value, wt. %	57.8	56.3	55.4	47.1
Ash, wt. %	0.07	0.14	0.13	0.03
Specific Gravity	1.336	1.32	1.318	1.225
Sulfur, wt. %	0.64	0.68	0.71	1.46

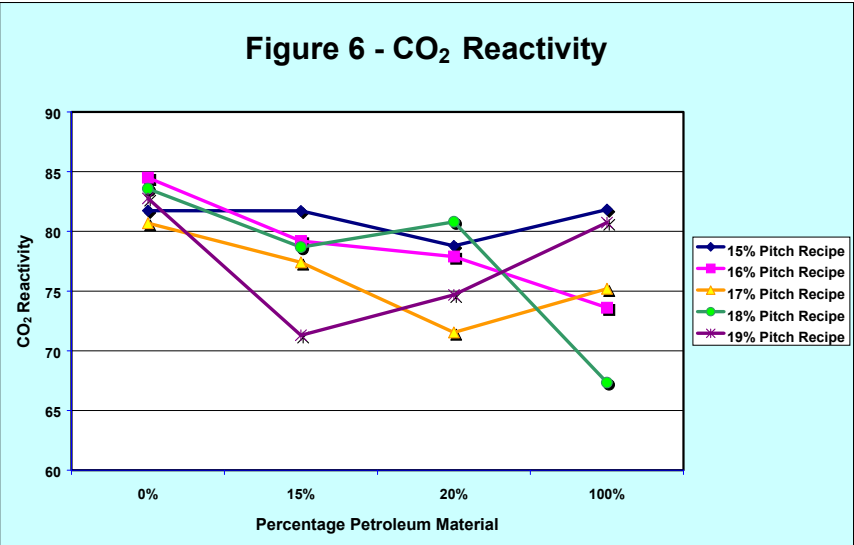
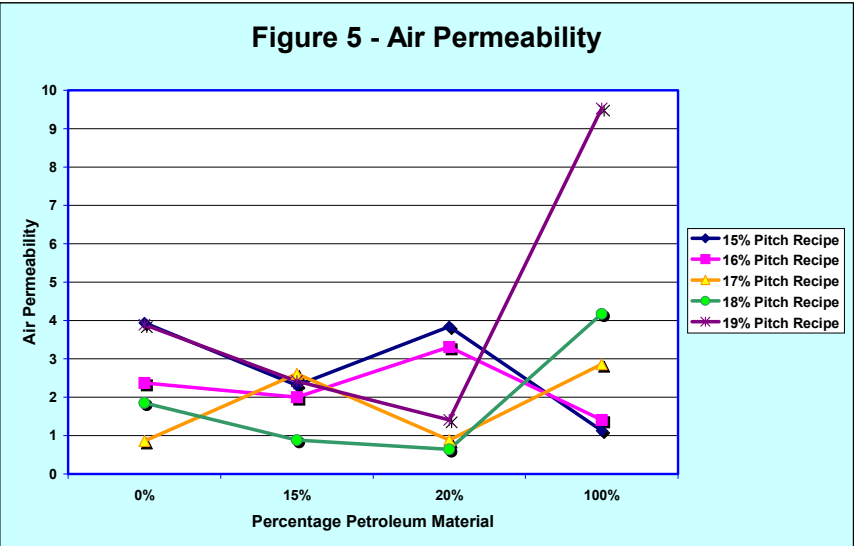
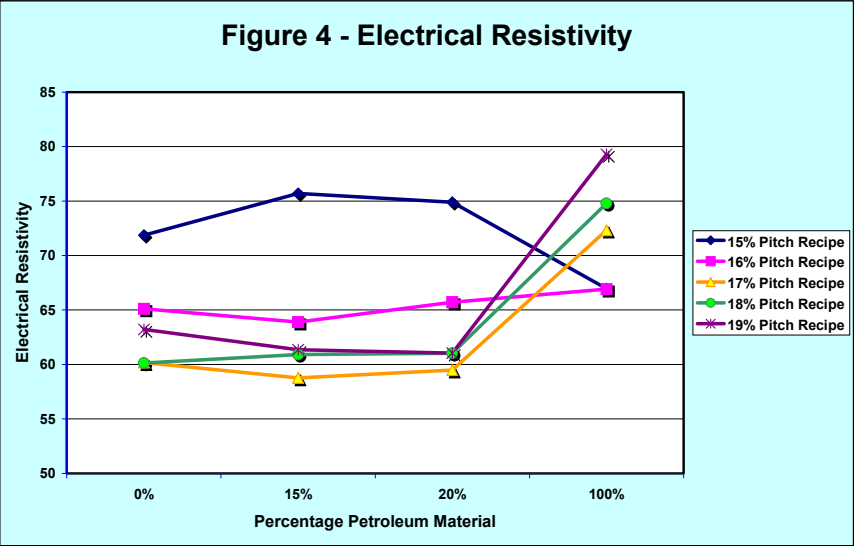
A series of laboratory size anodes was prepared using each of the four pitches. The details of the anode mixing, molding, and baking protocol are given in Table III.

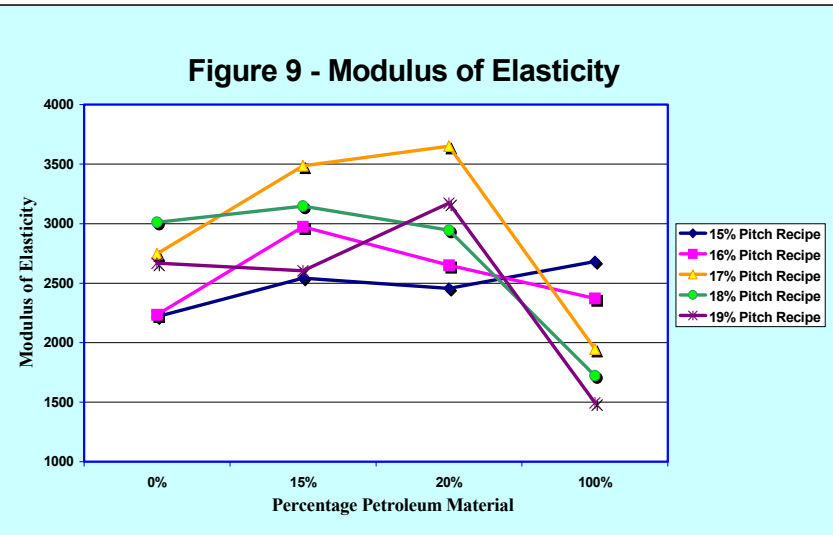
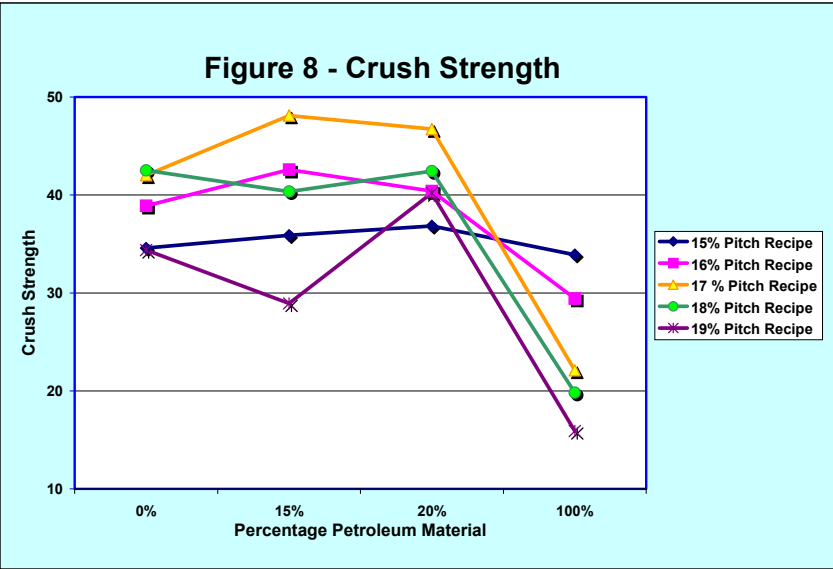
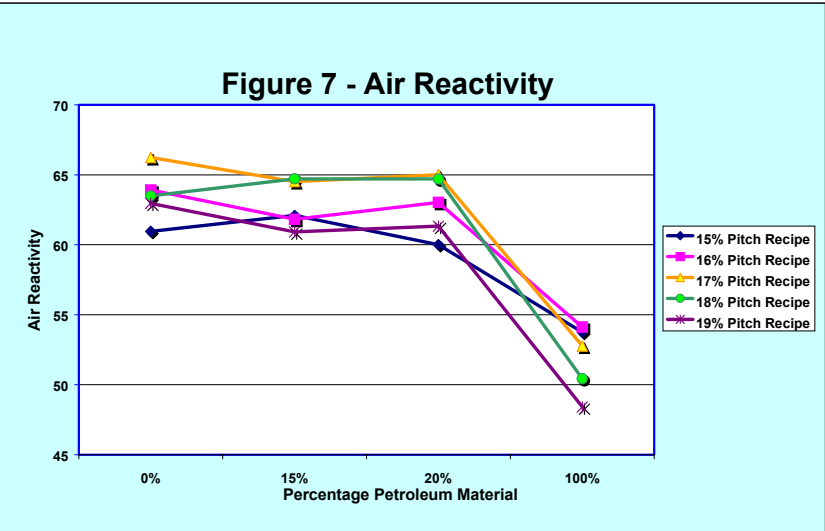
Table III – Anode Production Protocol

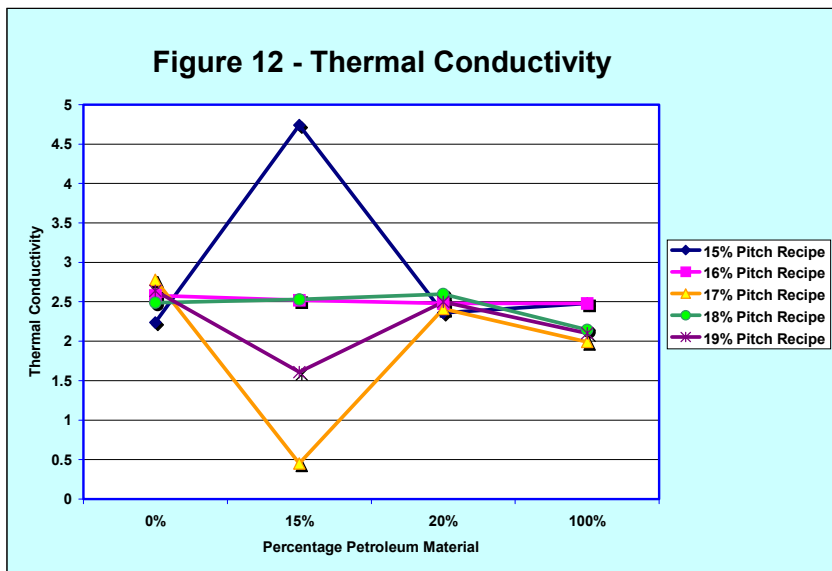
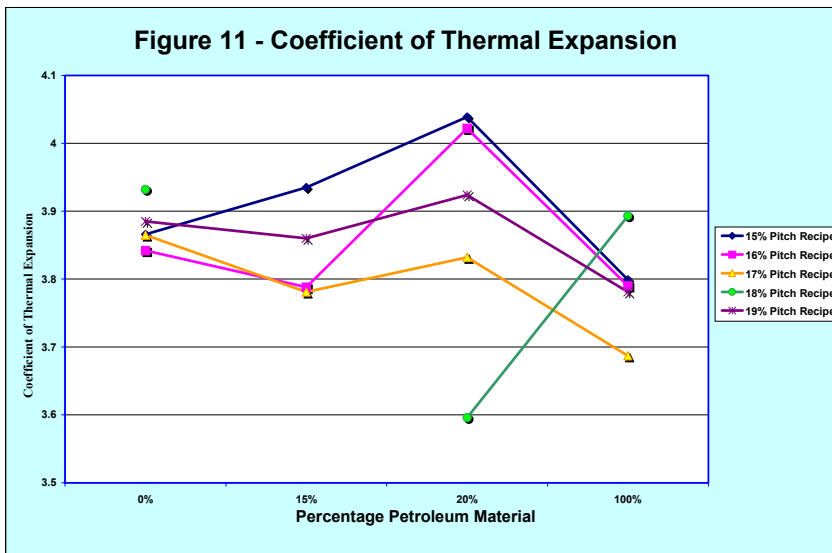
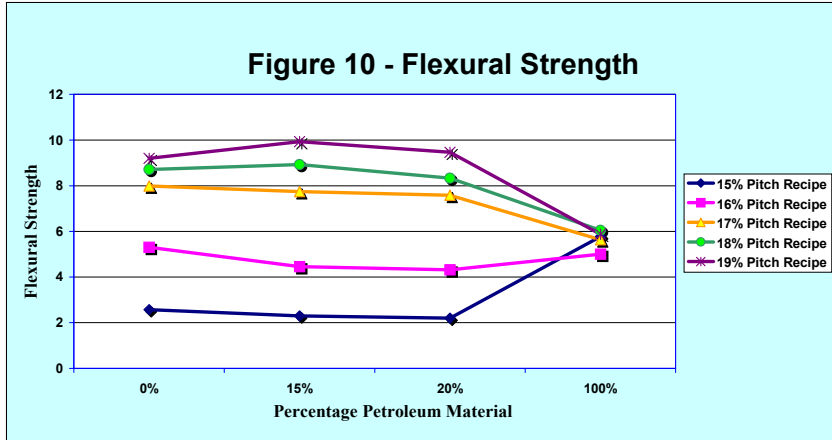
Binder Levels - 15%, 16%, 17%, 18%, and 19%	
Mixing and Molding Conditions	
Materials	Not Preheated
Mixing Time	19-25 Minutes
Mixing Temperature	159-163°C
Molding Temperature	149-153°C
Vibrating Time	65 Seconds
Baking Protocol:	
0-600°C	10°C/hr
600-1170°C	25°C/hr
1170°C	14 hr hold
Center Retort Temperature	1100-1120°C

After baking, the anodes were cored and the cores were tested for ten typical anode properties. Plots of the results of the testing are given in Figures 3-12. As the plots indicate, the coal tar/petroleum pitches produced anodes with equal or potentially improved properties. Koppers plans to continue its product improvement efforts in the area of petroleum-enhanced coal tar pitch.









The results of this laboratory anode study indicated that the reduced sulfur coal tar/petroleum pitch was an improved product. Several commercial trials of the product have confirmed the laboratory results. The results of one of these trials will be reported at the TMS meeting in San Diego, CA in February 1999. Koppers remains committed to its line of petroleum-enhanced coal tar pitch products and further efforts will be made to improve this product.

CONCLUSIONS

1. The supply of coal tar in North America is declining as a result of financial and environmental pressures resulting in the closing of coke ovens.
2. Coal tar pitch manufacturers are using a number of strategies including developing coal tar/petroleum pitches to deal with the coal tar shortage.
3. Petroleum-enhanced coal tar pitches which give equal and possibly improved performance to conventional coal tar pitch in aluminum anodes have been developed.
4. The use of petroleum-enhanced coal tar pitch is one of the preferred long-term solutions to the coal tar shortage because: 1) it is the most economical alternative, 2) the performance has been proven with over three years of commercial use, 3) the required petroleum material is readily available in North America and the supply has potential to grow with demand, and 4) a product of consistent quality is provided.

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