DEVELOPING COAL TAR/PETROLEUM PITCHES

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Abstract

Over the years the aluminum industry has evaluated the potential use of petroleum derived binders for producing anodes. Although this effort has been intense, unfortunately many of these evaluations produced less than desirable results. Initially economics drove these efforts, however in the future raw material availability and environmental regulations may drive the evaluation of all new raw materials. This paper will discuss the rationale behind developing coal tar/petroleum binder pitches including the future of coal tar pitch supplies, the potential environmental advantages of coal tar/petroleum pitches, and commercial experience with coal tar/petroleum pitches.

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 the building of by-product ovens, coal tar pitch has been the binder of choice for the aluminum, commercial carbon, and graphite industries.

Man has used another abundant raw material, petroleum, for centuries. The oil industry as we know it today began with the discovery of crude oil in Ontario and Western Pennsylvania in the 1850's. The complex facilities constructed to process crude oil have largely concentrated on producing transportation and heating fuels as their liquid products with little attention paid to petroleum derived binder materials. However, during the 1960's some refiners began to show an interest in producing petroleum derived pitches. These efforts resulted in the development of petroleum pitches that had reasonably high aromaticities and specific gravities. Evaluations of these petroleum pitches as binder pitch have given mixed results with the most often cited shortcoming being higher than desirable carbon consumption.[i, ii, iii, iv]

In the late 1980's and early 1990's the closing of United States coke ovens accelerated due to economic and environmental pressures. 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.[v] This paper will concentrate on the efforts to secure the future supply of binder pitch by developing an acceptable coal tar/petroleum binder pitch.

Discussion

Coal Tar and Petroleum 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 all pitch requirements well into the future.

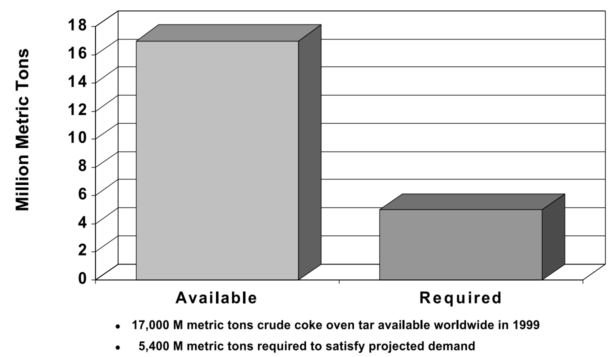

Figure 1 – World Coal Tar Supply

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 18% between 1997 and 2005 due to the factors discussed earlier.

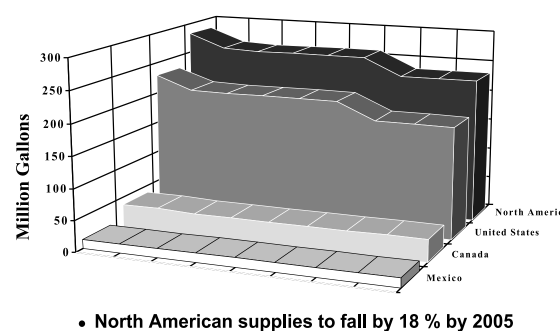

Figure 2 – North American Coal Tar Supply Trends

Table I gives North American coal tar pitch demand and coal tar requirements, availability, and deficits for 1997 and 1998 and predictions for 1999, 2000, 2001, and 2003.

Table I – North American Binder Pitch Demand

	'000 Metric Tonnes					
	1997	1998	1999	2000	2001	2003
Aluminum Industry	627	654	649	657	678	696
Commercial Carbon	108	112	95	100	108	115
Miscellaneous	170	160	159	140	127	100
Total	905	926	903	897	913	911
Coal Tar Required	1442	1555	1514	1517	1555	1570
Coal Tar Available	1302	1141	1141	1141	1027	1027
Tar Deficit	140	414	373	376	528	543

These predictions indicate the coal tar deficit will increase from 140,000 metric tons in 1997 to 543,000 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.

As has been clearly demonstrated in the previous discussion, strategies to deal with the declining American coal tar supply need to be implemented. One of these strategies is the use of coal tar/petroleum binder pitches. Toward this end Koppers began product development in the late 1980's to produce acceptable coal tar/petroleum binder pitches using petroleum pitches produced by Marathon Ashland Petroleum Company LLC. This strategy is particularly attractive since, as will be discussed next, there is an abundance of potential petroleum feedstocks. Also, considering the economics of other strategies, it is also the most economical.

In order to discuss comparative quantities of materials the coal tar supply is being converted to the traditional volume measure in the petroleum industry, the barrel. The total yearly supply of coal tar in North America is about 6 MM barrels. To put that number in perspective, that quantity is less than the volume of crude oil processed in the United States each day. Potential pitch feedstocks are derived from various refinery units including but not limited to thermal cracking, catalytic cracking, and specialty petrochemical units. The potential volume of pitch feedstocks from all sources is estimated to be 326,000,000 barrels per year. Assuming only 10 % of the potential feedstocks would be available for pitch production, this amounts to 32,600,000 barrels per year.

Coal Tar and Petroleum Pitch Manufacturing

Coal tar is a by-product of the coking of coal to produce metallurgical coke. Coal is heated to a temperature of approximately 1100°C in a coke oven to produce coke (the primary product) and by-products such as, coke oven gas, coal tar light oil, and coal tar. Typical yields are 70% solid products and 30% liquid products. The yield of coal tar, the feedstock for producing coal tar pitch, from a ton of coal is 30–45 liters (8–12 gallons). Coal tar pitch has many uses, but the majority of the pitch produced is used as a binder for petroleum coke to produce anodes and graphite electrodes. Figure 3 shows the flow scheme from coal coking to coal tar pitch production. As the flow scheme indicates coal tar pitch is produced by the distillation of coal tar.

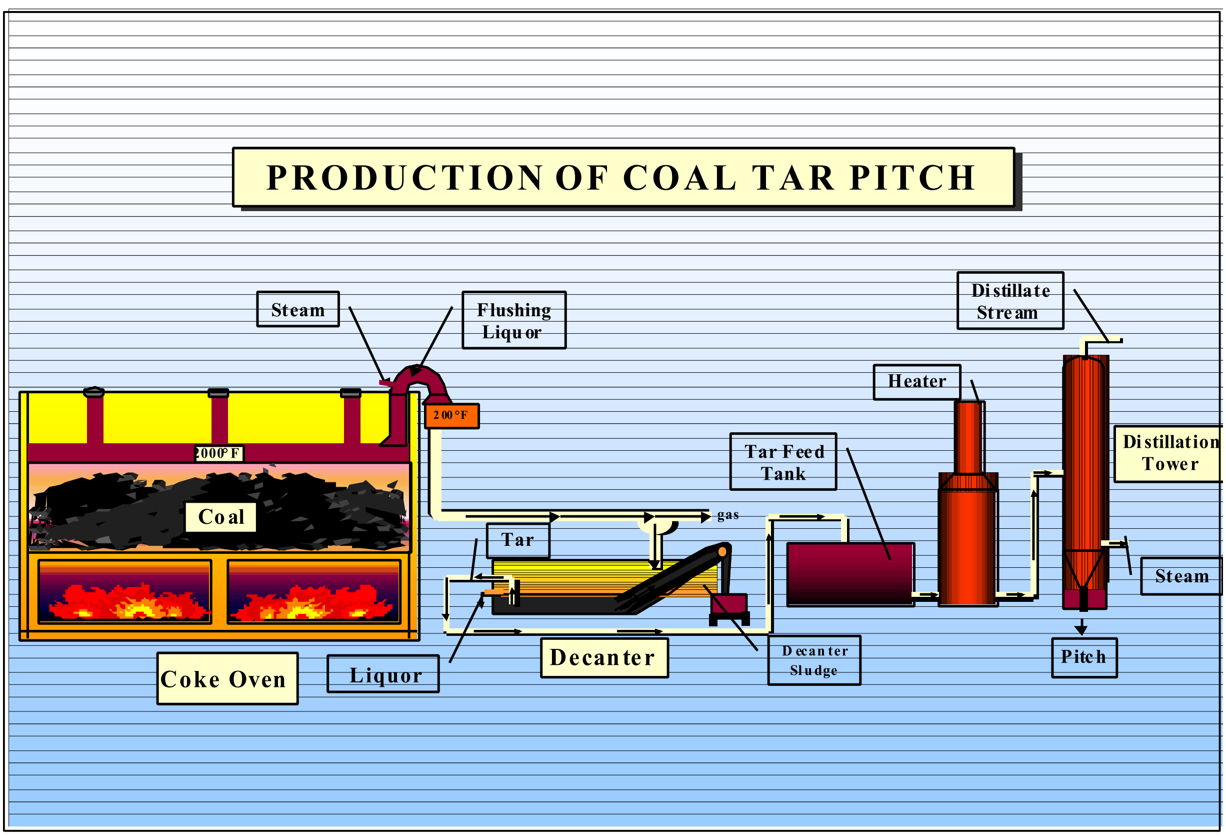

Figure 3. Coal Coking to Coal Tar Pitch

Many petroleum products are referred to as "pitch" by the petroleum industry. This fact has the potential to cause considerable confusion outside the refining community. In most cases, the different types of petroleum pitch share only the commonality of being black solids at room temperature. The individual characteristics of petroleum pitches vary as functions of feedstock and the specific processes used in their manufacture. Feedstocks can range from a predominantly aliphatic to predominantly aromatic type chemical structure. A reaction step is used to generate and/or concentrate the large molecules typically observed in petroleum pitch. The most common processes used to generate petroleum pitches are singularly or a combination of (a) solvent deasphalting, (b) oxidation, and (c) thermal processes.

Solvent deasphalting is used to separate fractions of various heavy oils. Solvent deasphalting involves mixing the feedstock with a paraffinic solvent such as propane, butane, or pentane. The mixing of the feedstock with these light paraffinic solvents causes precipitation of the molecules with higher molecular weights and aromaticities. The chemical and physical properties of this type of petroleum pitch are more closely associated with asphalt cements used for road paving. Typical properties include a specific gravity of approximately 1.0 g/cc at 60ºF, with the chemical composition containing significant amounts of non-aromatic hydrocarbons and high levels of iron, nickel, and vanadium.

Various grades of pitch can be produced by the oxidation of heavy petroleum hydrocarbons. Although oxygen is used in the process, the products typically do not contain significant amounts of oxygen. During this reaction, the presence of oxygen is successful in generating free radicals that induce polymerization reactions. The chemical properties of these products will depend upon the starting material and degree of reaction, but the pitches produced typically have low coking values and high viscosities.

Thermal processing is used to produce petroleum pitch as noted in several patents.[vi,vii,viii,ix] Thermal processing has traditionally been used to produce the high specific gravity and aromaticity petroleum pitches referred to in the introduction. The thermal processes typically employ heat treatment temperatures in the range from 300 to 480ºC. A typical flow scheme for producing petroleum pitch from crude oil by thermal processing is given in Figure 4.

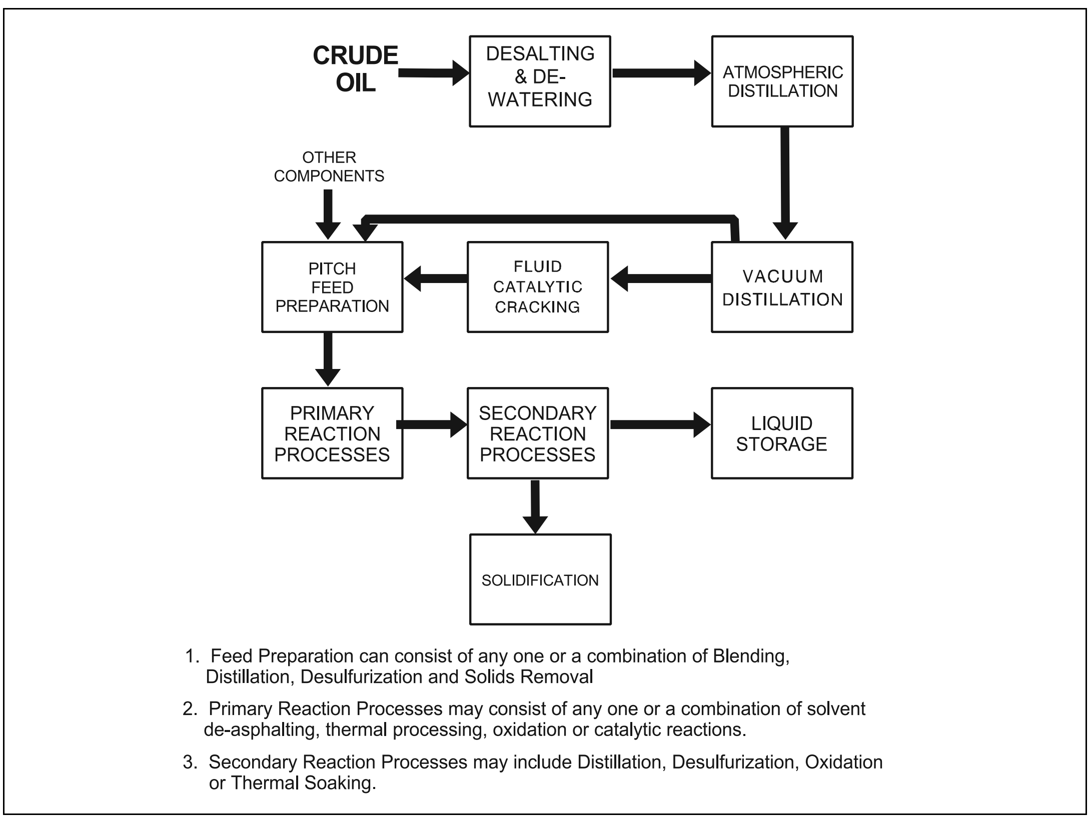

Figure 4. Crude Oil to Petroleum Pitch

Marathon Ashland Petroleum LLC uses a proprietary method for petroleum pitch production. The method produces a highly aromatic petroleum pitch containing few solids and a viscosity comparable with coal tar pitch. Properties of the pitch will be given in the next section.

Developing Coal Tar/Petroleum Pitches

In the late 1980's/early 1990's Koppers Industries adopted the development of coal tar/petroleum pitches as one of its strategies for dealing with the developing coal tar supply deficit. One of the leading concepts of the product development effort was that successful coal tar/petroleum pitch products employ coal tar and petroleum components whose properties are compatible. Furthermore, the composition and properties of the individual pitch components must be controlled to ensure final product quality. The first task of the product development effort was identification of an acceptable petroleum component for producing a superior coal tar/petroleum pitch. Approximately 100 petroleum materials have been evaluated during this program with the most favorable material identified being petroleum pitch produced by Marathon Ashland Petroleum Company.

The next task of the product development effort was identification of acceptable methods of combining the coal tar and petroleum components into the final binder pitch product. It was discovered that special care must be taken to obtain homogeneous product and appropriate processes were developed.

A very positive aspect identified during the development of coal tar/petroleum pitches is the opportunity to build on the positive characteristics of both the coal tar and petroleum components to produce a quality product with equal or improved properties. For example, the low sulfur content of coal tar pitch offsets the higher sulfur content of petroleum pitch and the low metals content of petroleum pitch offsets the higher metals content of coal tar pitches.

The product development effort took a dual product path with one product targeted for prebaked anode and graphite electrode binder applications. This product eventually contained approximately 15 % of the petroleum component and 85 % of the coal tar component. It was designed to perform in a similar fashion to the traditional coal tar binder pitch. The product has been designated Type A pitch. Typical properties of Type A pitch are given in Table II. The second product was developed specifically to reduce polynuclear aromatic (PNA) emissions from Soderberg plants. This product has been designated Type B pitch. Type B pitch is produced by a patented process[x] which results in a binder pitch which contains 40 % less PNA's than a typical coal tar pitch. Type B pitch is composed of approximately 40 % of the petroleum component and 60 % of the coal tar component. Typical properties of Type B pitch are given in Table II. A discussion of the development history of these two products follows.

After the final composition of Type A pitch was set, the next step was bench scale evaluation of the binding characteristics of the product with the production of laboratory anodes. Two separate bench scale evaluations were conducted. The first evaluation used pitch produced in the laboratory, while the second evaluation used pitch from a 200 ton batch of Type A pitch produced commercially. These bench scale evaluations gave very positive results, so plans were made to conduct commercial trials of Type A pitch. The first commercial trial of Type A pitch was a fourteen month trial conducted at a large smelter. During the trial 16,700 tons of Type A pitch were used to produce 115,250 vibroformed anodes weighing 908 kg each. The conclusions of the trial were that there were no significant differences between anode quality or performance when Type A pitch was used as the binder. A number of additional commercial trials indicated that Type A pitch was an acceptable product. Type A pitch is now a proven commercial product with about five years of commercial use.

The product development path of Type B pitch was similar to that of Type A pitch. After development of the final composition, bench scale evaluation of the binding characteristics of the product was performed with the production of laboratory anodes. Again, the bench scale evaluation gave very positive results, so plans were made to conduct commercial trials of Type B pitch. Unlike Type A pitch, Type B pitch has been evaluated commercially in both prebaked and Soderberg applications. The prebaked trail consisted of 520 tons of Type B pitch being used to produce 2,100 anodes weighing 825 kg each. The anode forming conditions were not adjusted for Type B pitch use and the trial anodes caused no significant problems with pot operation. However, average anode density and carbon consumption were slightly inferior for the Type B anodes. The Soderberg trail of Type B pitch consisted of the used of 1,000 tons of Type B pitch in a commercial Soderberg plant. The trail Soderberg anodes performed well, and a significant reduction in PNA emissions was realized. Presently Type B pitch does not have the extent of commercial use as Type A pitch.

Table II – Properties of Typical Pitches

Property	Coal Tar Pitch	Type A Pitch	Type B Pitch	Petroleum Pitch
Softening Point, °C	109.4	108.5	112.9	108.7
Toluene Insolubles, wt. %	27.5	25.8	29.6	3.5
Quinoline Insolubles, wt%	13.1	12.6	13.9	0
Beta Resins, wt. %	14.4	13.2	15.7	3.5
Coking Value, wt. %	57.8	56.3	58.4	47.1
Ash, wt. %	0.17	0.14	0.11	0.03
Specific Gravity	1.336	1.32	1.31	1.225
Sulfur, wt. %	0.64	0.68	0.78	1.30

As previously discussed, a second driver for the development of coal tar/petroleum pitches may be environmental regulations. Type B pitch was specifically developed to address this issue. Due to the lower processing temperature used to produce petroleum pitch the severity of thermal cracking achieved is much less. The reduced thermal cracking results in a product with a significantly lower PNA content. The benzo(a)pyrene (B(a)P) equivalent of coal tar and Type B pitches is given below:

Pitch Type	B(a)P Equivalent, ppm
Coal Tar	24,930
Type B	15,000

With the likelihood of increasing environmental pressures for the reduction of PNA emissions, Type B pitch may be the most economical alternative to achieve significant PNA reductions.

Conclusions

1. The supply of coal tar in North America is declining because financial and environmental pressures are resulting in the closing of coke ovens.

2. One of the strategies currently being used by coal tar pitch manufacturers to deal with the shortage of coal tar is developing coal tar/petroleum pitches.

3. Because the refining industry uses the name pitch for several refinery streams, many which have unacceptable properties to be a component of a coal tar/petroleum binder pitch, care must be taken to select a petroleum pitch with the desirable properties to produce an acceptable coal tar/petroleum binder pitch.

4. The use of coal tar/petroleum pitch is the preferred long-term solution to the coal tar shortage because: 1) it is the most economical alternative, 2) the performance has been proven with over five 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.

5. Coal tar/petroleum pitches produced using special manufacturing techniques have the potential to be the most economical route to significant PNA emissions reductions, especially from Soderberg operations.

6. Development efforts will continue to develop new and improved coal tar/petroleum pitch products.

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