COAL TAR PITCH – PAST, PRESENT, AND FUTURE

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Abstract

The first coal chemical recovery ovens were installed in the United States in 1893. By 1915, by-product ovens accounted for 97% of the metallurgical coke produced in the United States. These by-product ovens produced coal tar as one of the major by-products. An industry developed around distillation of coal tar to produce various products. One of the major products produced is coal tar pitch. Since that time, coal tar pitch has become the binder of choice for the aluminum, commercial carbon, and graphite industries.

A science has developed around defining the quality of a binder pitch based on its physical properties. Successful and unsuccessful efforts in this endeavor will be discussed. In addition some of the major changes in coal tar pitch properties as well as some of the successful and unsuccessful attempts to modify pitch properties will be discussed. Lastly, coal tar pitch supply and quality issues for the future will be addressed.

Past Lessons

Coal tar pitch has been the anode binder of choice for aluminum smelters since the inception of the industry. Coal tar pitch is produced from coal tar by a distillation process. In North America and Europe the majority of the anode binder pitch is produced by vacuum flash distillation.[1] In this process the tar is first atmospherically distilled to produce soft pitch which has a softening point of 80-90°C. The soft pitch is then distilled under vacuum to produce a pitch with a softening point of approximately 110°C. The process conditions necessary for producing this pitch are a temperature of 325°C and a residence time of 5 minutes. Figure 1 gives the material balance for coal tar pitch production using vacuum flash distillation.

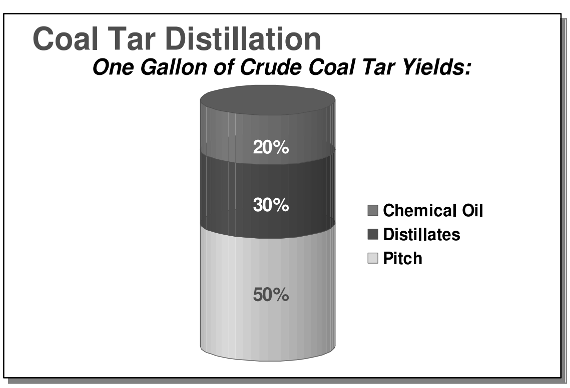

Figure 1. Material Balance for Coal Tar Distillation

The aluminum industry began to develop a group of physical and chemical properties of pitch that were important for the performance of pitch in producing quality anodes. Some of these properties included softening point, quinoline insolubles, toluene insolubles, density, coking value, ash, sulfur, and metals. Many of these pitch properties are dependent on the properties of the coal tar from which the pitch is produced. The coal tar distiller has two major tools for controlling pitch properties: 1) feedstock blending, and 2) distillation severity. Feedstock blending can be used to control such properties as quinoline insolubles, toluene insolubles, coking value, ash, sulfur, and metals; while distillation severity is used to control softening point. There is not a great deal of difference between the densities of coal tar pitches produced from high temperature coal tars. Figure 2 shows the relationship between pitch softening point and other pitch properties.

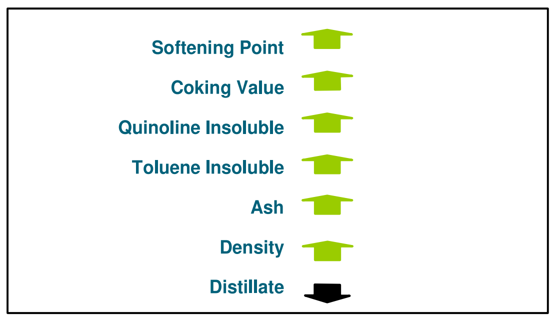

Figure 2. Pitch Property Interrelationships

Most of the values assigned to pitch specifications by smelters were derived from the properties of the pitch available in their local market. These values may or may not be optimal, but they matched the material that was available for use. Over the years these specification values have transitioned from a specification to a definition of quality. Such definitions are probably not valid. Table 1 shows the typical properties of pitches produced by Koppers in Australia, Europe, and the United States.

Property	North America	Australasia and China	Europe
Softening Point, °C	110-115	110-115	110-115
QI, wt.%	10-20	4-6	5-10
Coking Value, wt.%	53 min	52 min	55 min
Ash, wt.%	0.4 max	0.4 max	0.3 min
Specific Gravity, g/cc	1.3 min	1.3 min	1.3 min
Sulfur, wt.%	0.8 max	0.8 max	0.7 max

Table 1. Koppers Pitch Properties

It is evident from Table 1 that these pitches have some very different properties such as QI, but they are being used around the world to produce high quality anodes.

The pitch property that has received the most attention over the years has been quinoline insolubles. Coal tar pitch contains small particles that are insoluble in the strong solvent quinoline (hence the name quinoline insolubles or QI). These high carbon content particles are formed by the polymerization of coal volatiles during the high temperature coking of coal in metallurgical coke ovens. During distillation of coal tar almost 100 % of the QI in the tar is incorporated into the coal tar pitch product. Over the years the importance or lack of importance of QI on the quality of coal tar pitch for use as a binder has been reported in the literature. No clear conclusion regarding the importance of QI in determining the quality of coal tar pitch as a binder can be drawn from these reports [2]

A coke oven is operated by heating coal to a temperature of approximately 1100°C. As the coal is heated, it begins to emit coal volatiles. As a result of the loss of these volatiles, the coal shrinks in the coke oven. This shrinkage forms a headspace in the coke oven called the "tunnel head". The "tunnel head" is the reactor for the formation of normal QI. A photograph of the "tunnel head" is given in Figure 3.

Figure 3. Coke Oven Tunnel Head

There are two major types of QI present in coal tar or coal tar pitch as listed in Figure 4.

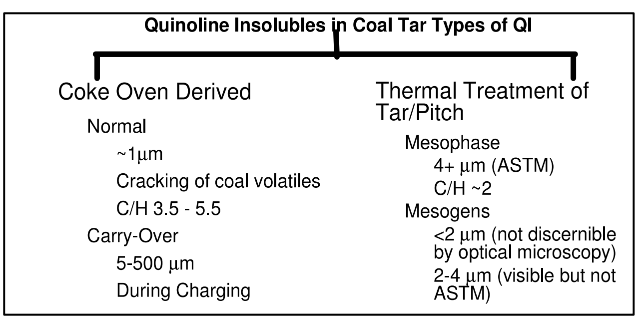

Figure 4. Types of QI

As shown in Figure 4, one type of QI is a result of coke oven operations, and the other results from the thermal treatment of the coal tar or coal tar pitch. Coke oven derived QI is divided into two types: normal, or primary QI, and carry over QI. Normal QI is formed by thermal cracking of the coal tar pitch volatiles in the coke oven. Normal QI has a very small particle size of approximately 1 micron and has a very high carbon to hydrogen ratio. Carry over QI is a result of the entrainment of solid particles in the coal volatiles as they are formed. Carry over QI includes ash, coal particles, and coke cenospheres. QI present in coal tar or coal tar pitch as a result of thermal treatment is called mesophase or secondary QI. The mesophase content of coal tar or coal tar pitch is determined by a test method designated as ASTM D 4616. The method uses optical microscopy under polarized light to examine a sample of polished pitch. Mesophase appears as multicolored spheres when viewed in this way. The ASTM method defines mesophase as any sphere with a size of greater than 4 microns. Mesophase has a much lower carbon to hydrogen ratio than normal QI.

Over the years there has been a trend around the world of gradually decreasing QI in binder pitches. These decreases can be explained by changes in coking coal type and coke oven operations. Figure 5 shows the effect of conditions in the "tunnel head" on the amount of normal QI formed.

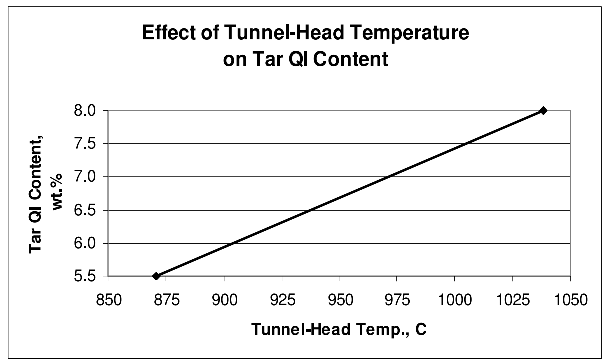

Figure 5. Effect of Tunnel Head Temperature on Tar QI Content

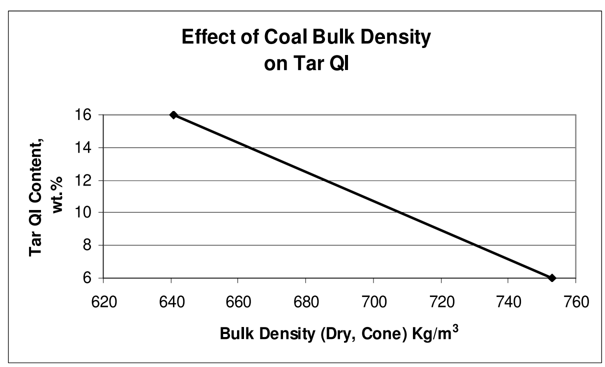

Figure 6. Effect of Coal Bulk Density on Tar QI

As Figure 5 and 6 indicate, there are two major factors which affect the amount of normal QI which is formed in the coke oven. These factors are the temperature in the "tunnel head" and the bulk density of the coal packed in the coke oven. The affect of temperature is easy to explain, but the affect of the bulk density of the coal is not as obvious. As mentioned previously, the formation of QI is a result of thermal cracking and polymerization of the coal volatiles in the "tunnel head". Therefore, it follows that an increase in temperature in the "tunnel head" would increase cracking and polymerization resulting in an increase in the amount of QI formed. The bulk density of the coal in the coke oven is inversely related to the size of the "tunnel head". Therefore, as the bulk density of the coal in the coke oven decreases the size of the "tunnel head" increases. As the size of the "tunnel head" increases, the residence time of the coal volatiles in the "tunnel head" increases. An increase in residence time causes an increase in the cracking and polymerization of the coal volatiles. This increases normal QI formation.

The discussion above shows that there is only one opportunity for the formation of normal QI in coal tar - in the tunnel head of the coke oven. Recreation of the tunnel head conditions outside a coke oven would be virtually impossible, if not impossible. Efforts over the years to increase the QI content of pitch by some sort of thermal treatment after the tar has left the coke oven have resulted in some dismal failures. These failures have been a result of the fact that the QI created is secondary QI (mesophase).

Present Situation

The present period has the potential to be the quiet before the storm for the coal tar distillation industries. That may seem hard to believe since we have reached where we are by struggling with a range of coal tar supply issues, coal tar QI issues, and the broad consideration of the use of coal tar as a fuel due to the high price of crude oil. Figure 7 shows the current and future projections for coal tar supply.

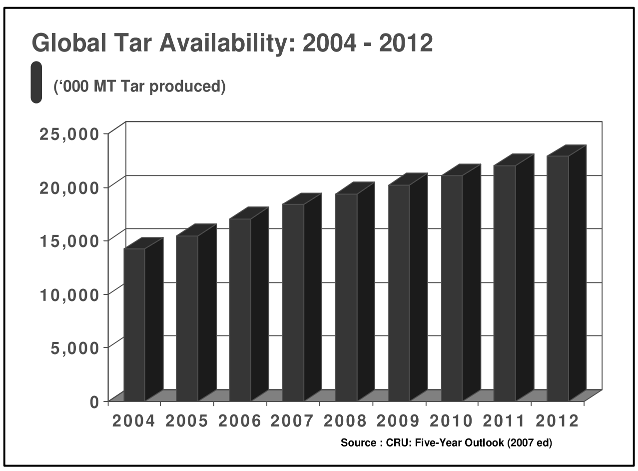

Figure 7. Current and Future Coal Tar Supply Projections

Figure 7 indicates that the global supply of coal tar has grown at a steady pace since 2004. When considering the global coal tar supply situation, however the source of the tar must be considered. As indicated in Figure 8, in 2007 about half of the coal tar in the world was produced in China.

The shift in coal tar supply shown in Figure 8 has resulted from two factors: 1) The rapid growth of the steel industry in China, and 2) The closing of many European and North American coke ovens during the 1980's and 1990's. These factors have resulted in some interesting developments: 1) Coal tar/petroleum pitches are now widely used in North America [3], and 2) Pitches with QI's lower than ever are being used to produce high quality anodes. As will be discussed in the next section the growing coal tar supply in China will drive the growth of anode binder pitch supply going into the future.

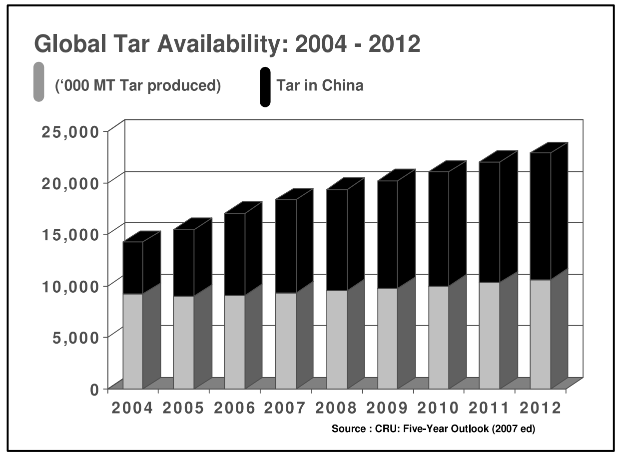

Figure 8 Source of Global Coal Tar Supply

Future Challenges

It is now time to look into the crystal ball. It is projected that the three driving forces for coal tar pitch issues in the coming years will be: 1) The projected rapid growth in aluminum production, 2) Continued increases in cell operating amperages, and 3) The increasing concern for human exposure to coal tar pitch volatiles. The remainder of this paper will discuss these issues.

The projected growth in aluminum production is shown in Figure 9.

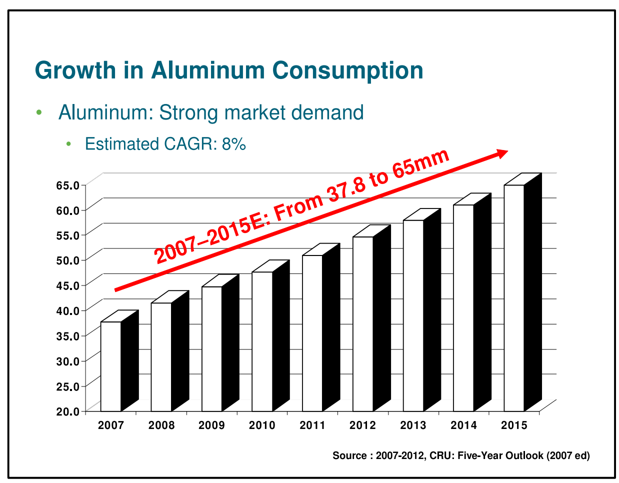

Figure 9. Growth Projection for Aluminum Production

As Figure 9 indicates, significant growth in aluminum production is projected with an estimated compound annual growth rate of approximately 8% looking out to 2015. This additional metal production will increase the demand for pitch. From a historical perspective, the pitch demand growth projection from the additional metal production is a very high-growth demand curve. This results in the question - "where will the industry get this additional pitch from?" Figure 10 gives the projected global coal tar supply position out to 2012.

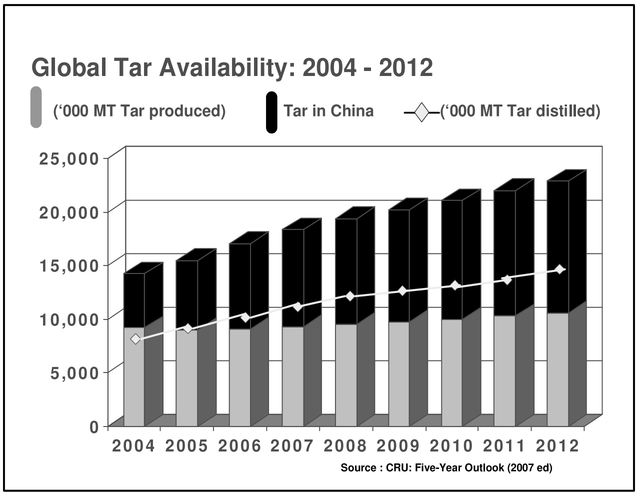

Figure 10. Global Coal Tar Projections

In Figure 10, the (white) line indicates the amount of tar required by the global coal tar distillation industry. The volume of tar above the line is all consumed, as either carbon black feedstock or liquid fuel. This figure shows some important points. In 2005, the global tar distillation market required the equivalent of all of the non-Chinese coal tar produced. As we proceed from 2005, the reliance on Chinese tar resources continues to escalate. With the vast majority of new coke ovens being built inside China, much of the binder pitch required to support aluminum growth will be produced from Chinese coal tar. While the bottom line is that there is sufficient coal tar in the world to supply the binder pitch required by the aluminum industry, the shift is clearly towards more reliance on Chinese tar. The big question is "what are the characteristics of Chinese coal tar?"

Chinese coal tar is quite different than most other coal tars in the world. First, Chinese coal tar is low in primary quinoline insolubles content. The low QI content of Chinese coal tar is a result of lower temperature metallurgical coke oven operations and other coke oven operating procedures.

Currently China uses two very different processes to produce coal tar pitch. One process is vacuum distillation, the process that Koppers uses in all of its facilities around the world. Vacuum distillation produces a pitch with approximately double the QI content of the tar distilled to produce the pitch. The majority of Chinese tars would produce pitches with QI contents of 3 wt. % to 5 wt. % with vacuum distillation. Vacuum distillation subjects the pitch to low temperatures for a short time so no mesophase (secondary QI) is produced. The second pitch production process used in China produces a product called modified pitch. It is a heat treatment process with no or minimal vacuum. The modified pitch process subjects the pitch to high temperatures for a relatively long time. The formation of mesophase while the pitch is exposed to the higher temperatures for a significant amount of time results in significant increases in the QI content of the modified pitch.

The nature of the coal tar and the pitch production processes used in China mean that anode producers will be faced with two significant binder pitch questions. The first question is -"How much QI is necessary for a quality anode binder pitch?" Since becoming involved in the Chinese coal tar industry, Koppers has done considerable work to understand the QI content necessary for a quality binder pitch. This work has caused many in Koppers to change their opinion concerning the amount of QI necessary to produce quality anodes. This work has led to the conclusion that some QI is necessary for a quality binder pitch, and that a primary QI content of 4 to 5 wt. % is quite acceptable. The second question is – "what is the effect of mesophase on binder pitch quality?" Modified pitches in China contain 2 to 10% mesophase, some of fairly large particle size. Many literature references report that mesophase has several negative effects on anode quality. Generally speaking, these effects are caused by the negative impact of the mesophase particles on the mixing and baking processes, resulting in difficulty in determining optimum pitching levels in the carbon plant. One of the big questions carbon plant personnel will have to answer is - "Do you want to use a pitch with a QI close to what you are familiar with, but contains mesophase, or would you rather have a non-mesophase containing pitch with a lower QI content?"

The most significant trend in smelter technology at present is increasing cell amperage. Increasing amperage is occurring at both the greenfield and brownfield level. Significant development activities in increased cell amperage are being conducted by a number of companies including Rio Tinto Alcan, Alcoa, Rusal, Dubal, and several Chinese companies. The trend to higher cell amperage results in several operating advantages including more efficient use of electricity, reduced emissions, and greater aluminum production in each cell. On the basis of these advantages and the wide dispersion of available technology, we expect that most if not all new smelter projects will be based on high amperage cells. Figure 11 shows the percentage of aluminum produced in cells operating at amperages less than 180kA is 42.5%, in cells operating between 180 kA and 300 kA is 36.2 %, and in cells operating at amperages greater than is 300 kA 21.3 %. It also shows that if we assume that 100 % of the new aluminum production brought on line from 2007 to 2015 will be at amperages greater than 300 kA, the percentage of aluminum produced in cells operating at amperages greater than 300 kA will jump from 21.3% to 54.1 %.

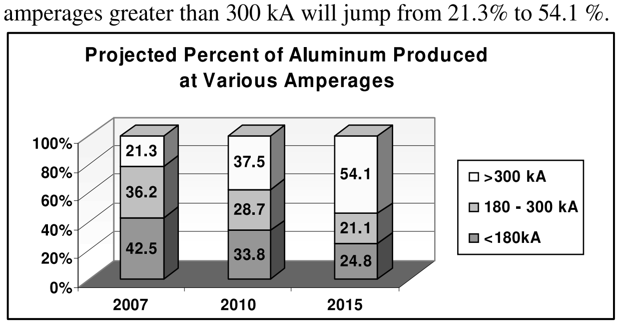

Figure 11. Aluminum Cells Operated at Various Amperages

Figure 12 shows the amount of aluminum produced at the three amperage ranges. Currently the amount of aluminum produced in cells operating at amperages less than 180kA is 16.2 million metric tonnes, in cells operating between 180 kA and 300 kA is 14.0 million metric tonnes, and in cells operating at amperages greater than is 8.2 million metric tonnes. Again, if 100% of the new aluminum production brought on line from 2007 to 2015 operates at amperages greater than 300 kA, the amount of aluminum produced in cells operating at amperages greater than

300 kA jumps from 8.2 million metric tonnes to 35.0 million metric tonnes.

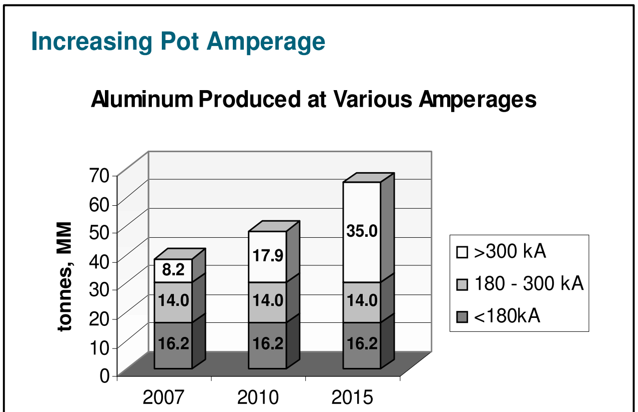

Figure 12. Percent of Aluminum Produced at Various Amperages

This trend toward higher cell amperages will have a definite and important effect on the quality of the anodes needed. Cells operating at higher amperages are less tolerant to anode imperfections. This intolerance is caused by greater heat being generated in, and transferred through, the anodes resulting in increased anode airburn and greater sensitivity to anode cracking problems. In turn, the need for more consistent and better quality anodes means that higher quality raw materials, including binder pitch, will be required.

The need for better quality anodes and reduction of human exposure to coal tar pitch volatiles will lead to the investigation of higher softening point pitches in the future. [[4]] Table 2 gives the coking value, volatiles content, and PAH content of the volatiles for several coal tar pitches of increasing softening points.

Softening Point, °C	Coking Value, wt.%	Volatiles, wt.%	Volatiles PAH's, ppm
111.4 (CT)	57.4	59.56	88100
139.0 (CT)	64.3	53.61	67100
150.6 (CT)	67.4	51.17	41600
165.2 (CT)	71.6	46.71	30900
112.3 (Type B)	57.0	58.78	26700
122.1 (P)	49.9	65.86	18900

Table 2. Physical Properties of Various Softening Point Coal Tar Pitches. (CT = Coal Tar pitch, P = Petroleum pitch, Type B = blend of CT and P)

This table shows that as the pitch softening point increases, coking value increases and volatiles content and PAH content of the volatiles decrease. In addition to reduced human exposure to coal tar pitch volatiles, these pitches have great potential to increase anode quality because of their increased coking value. The increased binder pitch coking value should result in increased anode baked density and the resultant improvement in other anode properties. The reduced amount of volatiles produced during anode baking should also allow for a faster anode baking cycles, resulting in reduced costs per tonne of anode produced.

Conclusions

- Over the years, binder pitch specifications developed around local pitch supply have transformed into definitions of global binder pitch quality.
- The pitch properties which indicate good pitch quality vary significantly around the world.
- The growing aluminum industry will depend heavily on coal tar pitches produced from coal tar from China.
- The trend toward increasing cell amperage will result in a need for higher quality anode raw materials.
- Investigation of higher softening point coal tar pitches should be conducted because of the potential for improved anode quality and reduced human exposure to coal tar pitch volatiles.

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