

EFFECTS OF TAR QUINOLINE INSOLUBLES ON MANUFACTURED CARBON PERFORMANCE

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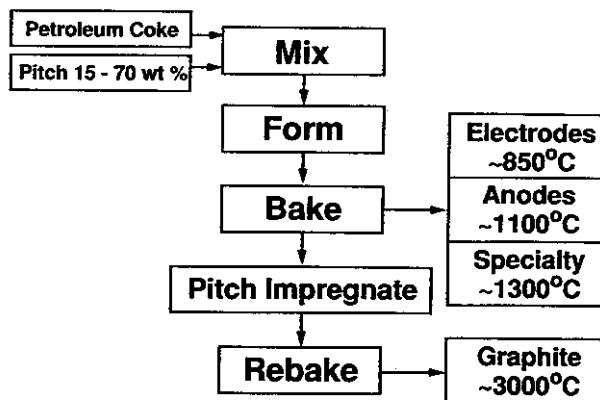


Fig. 1. Preparation of Carbon/Graphite

INTRODUCTION

Coal tar pitch is used as a binder in the manufacture of various carbons such as: a) graphite electrodes for the steel industry, b) carbon anodes for the aluminum industry and c) specialty carbons such as bearings, seals and piston rings [1]. Basically, the manufacturing process consists of mixing a filler material (usually calcined petroleum coke) with pitch, forming the mix and baking this green mix to about 850-1300°C (electrodes 850°C, anodes 1100°C and specialty carbons 1300°C), Figure 1. In some cases the baked carbon is impregnated with pitch (usually petroleum pitch) and rebaked to increase its density. The production of graphite requires heating the baked and impregnated carbon to about 3000°C. The amount of binder used varies from about 15 to 70 weight percent depending on the type of product being produced; electrodes require about 20 weight percent, anodes about 15 weight percent and specialty carbons about 35 to 50 weight percent and sometimes as high as 70 weight percent.

Binder pitch is produced by removing the lower boiling components of coal tar through distillation until the residue (pitch) reaches a softening point (SP) of about 110°C [2]. The yield of pitch is normally about 50-55 weight percent. Binder pitch is characterized by several standardized tests such as SP, quinoline insolubles (QI), toluene insolubles, coking value, ash, and distillate content to 360°C. One of the more important properties of binder pitch is the QI content. The object of this paper is to describe the analysis, formation and impact of QI on the performance of electrodes and anodes.

ANALYSIS OF QI

The total amount of solids in tar or pitch can be determined by one of several standardized tests. Essentially, they consist of digesting tar/pitch in a solvent then filtering the mixture, washing, drying, and weighing the filter cake [3]. Besides quinoline, other solvents such as anthracene oil and 1-methyl-2-pyrrolidinone [4] can be used and give results comparable to quinoline. In some cases, a filter aid such as diatomaceous earth is added to facilitate the filtration. The extracted QI material can be further characterized as to type or origin by reflected polarized light microscopy (petrography) which requires mounting the solids in epoxy resin and polishing the mounted sample [5,6]. Other microscopic techniques such as scanning and transmission electron microscopy are also used to study QI [7-9].

TYPES OF QI

There are essentially two types of QI that are formed during the coking of coal: primary and carry-over.

Primary quinoline insolubles are formed by cracking coal volatiles when they encounter the high temperatures (about 1100°C or 2000°F) of the coke mass, oven walls, and tunnel head. Primary QI particles are similar to carbon black and about 1 micron (μm) or less in diameter. A photomicrograph of extracted primary QI using scanning electron microscopy (SEM) is shown in Figure 2.

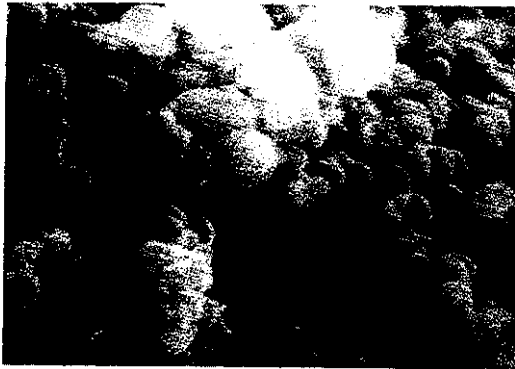


Fig. 2. Photomicrograph of primary QI extracted from pitch (Scanning electron microscopy, X 12000).

Unlike primary QI, carry-over QI does not involve cracking of volatiles during coal carbonization but the mechanical transport of coal and coke particles in the by-product collection system. However, since the introduction of steam aspiration, carry over has increased significantly during the charging of ovens. Most of these particles are coke cenospheres which are formed as coal particles soften, assume a spherical shape and rapidly devolatilize forming a spherical, fairly hollow coke structure as shown in Figure 3. The photomicrograph shown in Figure 3 was



Fig. 3. Photomicrograph of pitch showing primary QI surrounding a cenosphere (Reflected polarized light microscopy, X 300).

taken using reflected polarized light microscopy of a polished pitch sample; this pitch sample, of course, also contains primary QI and the appearance of primary QI as revealed by light and scanning electron microscopy can be easily compared by referring to Figures 3 and 2. Note that the magnification of Figure 2 is much greater than in Figure 3. The cenosphere in Figure 3 is about 50 microns in diameter and intact. Cenospheres range in size from about 20 to 500 microns and in many cases the cenospheres break and pieces of the cenospheres are seen during petrographic analysis.

Particles of coal and non-coal-related mineral matter can also be carried over. Coal-related mineral matter is mostly clay, pyrite and quartz; non-coal-related mineral matter is essentially particles of oven refractory and luting compounds such as quartz and clay used to seal the doors and coal charging holes.

Coal tars contain about 2 to 12 weight percent of total QI depending on coke type and production conditions. Typically, about 80 to 90 percent of the total QI is composed of primary QI. The balance is composed primarily of cenospheres with a small concentration of other carry-over particles (such as coke, coal and minerals) and other volatile-derived particles (such as pyrolytic carbon and pitch coke). Like primary QI, pyrolytic carbon is derived from the decomposition of coal volatiles but ranges in size from a few to several hundred microns; pyrolytic carbon is similar in appearance to other carbon deposits found in coke ovens such as roof and wall carbon. Pitch coke is formed by the carbonization of tar/pitch.

There is a third type of QI called mesophase (or secondary QI) which is not formed in the coke oven but by thermal treatment of tar or pitch [7]. Since tars/pitches are not normally thermally treated in North America, binders produced in North America from domestic tars do not contain mesophase. More detailed descriptions of the various types of QI and carbon forms can be found in References 5, 6 and 10.

Primary QI is very beneficial, if not essential, to the satisfactory performance of anodes and electrodes; however, the amount of primary QI must be consistent. On the other hand, carry-over QI is of no benefit whatsoever and its concentration should be kept as low as possible. The positive effects of primary QI and the negative effects of carry-over QI are explained in more detail below.

POSITIVE EFFECTS OF PRIMARY QI

Binders function primarily by forming pitch coke bridges between the filler petroleum coke during the baking process. How the binder pitch coats and penetrates petroleum coke particles during mixing and forming and how the pitch converts to pitch coke bridges during baking have a great impact on the properties and performance of the carbon. QI plays a very important role in how pitches perform these functions.

To better understand how petroleum coke particles interact with pitch, mixes of petroleum coke and pitch have been examined petrographically at magnifications up to 1000. It has been observed that pitches containing about 10-15 weight percent QI coat or "butter" petroleum coke particles much better than pitches containing about 1 or 2 weight percent QI [11]. In addition to enhancing the coating of the petroleum coke particles, QI also controls the penetration of pitch into petroleum coke pores so that excessive pitch is not required and that the pitch coke bridges are "well anchored" to the petroleum coke particles [12]. Obviously, carbons that are composed of petroleum coke particles that have well developed pitch-coke bridges will have improved properties over carbons with poor pitch coke bridges.

As explained previously, the "green" carbons containing pitch and petroleum coke are baked to temperatures between 850 and 1300°C and electrodes are further heated to about 3000°C to form graphite. During baking, binder pitch is converted to pitch coke and during this process about 40 weight percent of the pitch is volatilized and escapes from the carbon. Primary QI plays an important role during the baking process in that it helps provide "paths" which facilitate the escape of volatiles from the pitch binder. These "paths" help reduce cracking and consequently can increase strength and decrease resistivity [12]. Also, during baking, the conversion of pitch to pitch coke is increased by two mechanisms: a) the primary QI has a high coking value (CV) and b) primary QI may provide sites for coke formation so that the amount of pitch coke formed is greater than would be expected from the sum of the CV of the pitch and the QI [13].

Primary QI also causes the formation of isotropic pitch coke bridges which are stronger than the anisotropic pitch coke that would be formed in the absence of primary QI. This isotropic pitch coke affects the electrical resistivity [14-21]; the interaction of strength and

resistivity will be discussed in the next section.

The importance of primary QI in binder pitch is well established; however, there is some disagreement as to the optimal content. There are reports that favor lower levels such as 5-10 weight percent while others favor levels up to 20 weight percent [22-26]. However, all agree that whether high or low, a consistent level of primary QI is important. Extremely high levels of primary QI can increase the extrusion pressure of a graphite electrode mix [27] and the development of cross cracks in the electrode which can degrade performance.

Generally, manufacturers of carbon anodes for the aluminum industry and graphite for the steel and specialty industries prefer a primary QI concentration range of 13 to 16 weight percent in the pitch. Since pitch yield is normally about 50-55 weight percent, the 13-16 weight percent pitch QI translates to roughly 7 to 9 weight percent in dry tar.

VARIATION IN TAR/PITCH QI CONTENT

Typically, binder pitch specifications have a range of 5 percentage points (e.g. 10-15 or 13-18 wt%). However, with increasing use of statistical process controls, many consumers of coal tar pitch are requesting a 3 percentage point range, which translates to a tar QI range of about 1.5 percentage points. A plot of the variation (from the annual average) of the QI content of tar produced at one coke plant during 1990 is shown in Figure 4. It is seen in the plot that the QI varied about 10 percentage points which is considerably beyond the desired 1.5 percentage point range making it at times very difficult to meet customer consistency requirements (the desired range is indicated on Figure 4 by lines 0.75 percentage points above and below the average). The QI plotted in Figure 4 reflects both primary and carry-over QI since it was determined by the ASTM solvent extraction method and the amounts of the two types of QI were not determined petrographically. However, the changes in QI were mostly due to changes in primary QI since changes in the ash content of the tar were small in relation to the changes in total QI, Figure 5.

The need for a consistent QI content can be illustrated by the effect of primary QI on two important characteristics of a graphite electrode, namely, electrical resistivity and strength. Resistivity

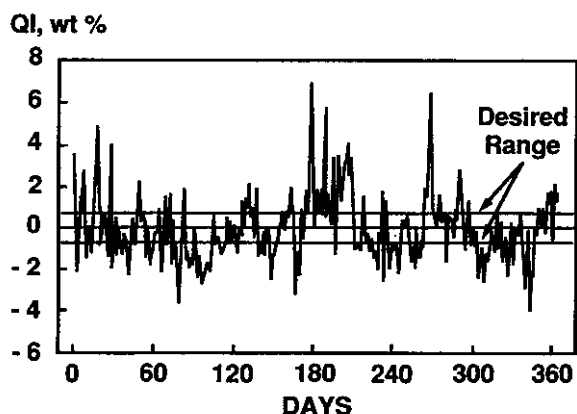


Fig. 4. Deviation from average tar QI (1990).

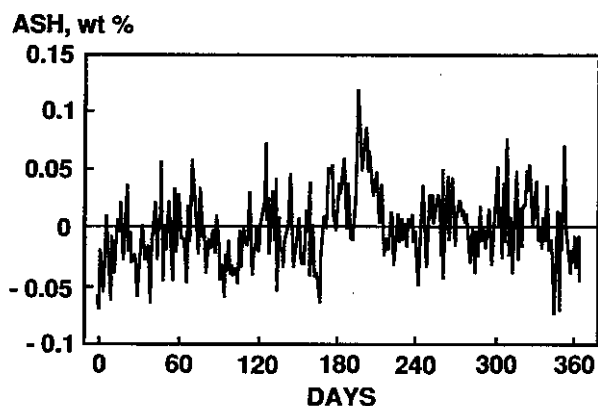


Fig. 5. Deviation from average tar ash (1990).

should be low since the high electrical current in the electrode will increase the temperature of the electrode due to internal resistive heating. Increased electrode temperatures increase the oxidation rate and decrease the current carrying efficiency of the graphite. The strength of the electrode must be sufficient to prevent its breakage while in use. Also, a decrease in strength of the graphite nipples used to connect electrodes can be quite costly since a failure of a nipple will cause 1 or 2 electrode segments to fall into the molten steel bath; these pieces must, of course, be retrieved from the 1600-1800°C bath. Obviously, high resistivity, high graphite oxidation rates, and breakage while in use can greatly increase operating costs. As mentioned earlier, QI affects electrode resistivity since it alters the

structure of the pitch coke bridges between petroleum coke particles and the altered structure (isotropic) has a higher resistivity. However, the isotropic pitch coke is stronger than anisotropic pitch coke and this fact can increase the strength of an electrode. Strength and resistivity can be balanced by carefully adjusting the petroleum coke granulometry and other processing conditions to the specific QI content of the pitch. This is a slow process since the elapsed time from initial mixing of petroleum coke and pitch to a finished graphite electrode is about 3 months. The adjustments in processing conditions allow the use of a low-QI pitch such as 5-7 weight percent or a higher-QI pitch such as 12-14 weight percent. However, a change of 3-4 percentage points in the QI level can effect the quality of the electrode necessitating changes in processing conditions the effect of which on the final product may not be seen for several months [28]. Since it may take several months to adjust to a new pitch QI level, periodic changes in QI concentration will hinder the efforts of the electrode producer to attain a stable process.

A process change typically made to compensate for QI variations in pitch is to vary the pitch content of the petroleum coke pitch mix. Usually for a decrease or increase of 5 to 10 percentage points of QI in the pitch, the binder pitch content is decreased or increased one percentage point, respectively, to maintain optimum properties in the manufactured carbon [18,29].

NEGATIVE EFFECTS OF CARRY-OVER QI

As previously explained, a consistent concentration of primary QI improves the quality of manufactured carbon and graphite. Conversely, carry-over QI has only negative impacts on carbon/graphite quality; the higher the carry-over QI content the more detrimental the effect. The ash content of pitch is due almost exclusively to carry-over QI and constituents of the ash such as sodium, vanadium, and iron can increase the loss of carbon and thereby increase cost due to increased oxidation during use [30,31]. These metallic contaminants act as catalysts and decrease the life of the carbon. Carry-over materials such as silicon can become incorporated in aluminum and cause problems during extrusion of the metal. Also, carry-over QI can increase the resistivity of carbon/graphite, thereby, increasing the energy required to produce aluminum and steel and again the cost. Coal particles in the pitch are undesirable since they devolatilize during baking

causing voids. In short, carry-over QI does nothing to improve the quality of carbon/graphite and should be kept at as low a level as possible.

The carry-over QI particles are also undesirable since they settle in tar and pitch storage tanks, resulting in tank heels, and are highly abrasive to process equipment, such as pump impellers and piping.

As mentioned previously, carry-over QI is identified and quantified using petrographic techniques which are time consuming and expensive. However, under normal operating conditions, the amount of carry-over QI can be estimated by the ash content of the tar since most ash-forming materials in the tar are carry-over related.

CONCLUSIONS

1. Consistent primary QI within a range can improve the quality of carbon anodes and graphite electrodes thereby decreasing the cost of making aluminum and steel.
2. Carry-over QI is detrimental to both the end users performance of carbon and graphite products, and operations of tar distillers and carbon/graphite manufacturers where carry-over QI settles in tanks, and increases wear of process equipment. Therefore, its concentration should be as low as possible.
3. Unless tar distillers have consistent sources of tar at the proper QI, they may soon find themselves incapable of meeting the requirements of their customers. Only consistent tar QI will allow tar distillers and their customers to continuously improve product quality.

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