Process Development for Production of Hard Pitch from Coal Tar for Electrode Industries

A. J. CHAUDHURI, Harihar SINGH¹⁾ and L. PARTHASARTHY²⁾

R & D Centre, SAIL, Bokaro Centre, Bokaro Steel Plant, Bokaro Steel City-827011, Bihar, India.

1) Bokaro Steel Plant, SAIL, Bokaro Steel City-827011, Bihar, India.

2) Coal, Coke and Chemicals Division, RDCIS,

SAIL, Ranchi-834002, Bihar, India.

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Coal tar pitch is a residue of coal tar distillation and can be processed suitably to produce hard pitch of desired quality in terms of softening point (SP), benzene insoluble (BI), quinoline insoluble (QI), β -resin and coking value (CV). As per customer requirement, these properties could be achieved by controlling coal tar quality, different parameters during distillation of tar and processing of soft and medium pitch. Coal tar pitch with CV in the range of 55–58%, BI content of 30–32%, QI content of 13–16% and SP of 95–105°C, finds its use as a binder for manufacture of electrodes.

During 1993, Bokaro Steel Plant (BSL), SAIL produced poor quality coal tar with high BI and QI content in it due to poor health of coke oven batteries. The by product plant, found it difficult to produce hard pitch to the specification of aluminium and electrode industries. The R & D Centre at SAIL in association with BSL undertook a project of process development for converting high BI and QI content tar to hard pitch by blending it with low BI and QI tar from other plants in an appropriate ratio, modifying operating procedure (tar flow rate to pipestill, second stage evaporator temperature, air flow rate & temp. of soft pitch in a batch reactor) to the customer's requirements. Bokaro Steel Plant produces and sells about 3000 t/year of hard pitch to electrode industries.

KEY WORDS: softening point; benzene insoluble; quinoline insoluble; β -resin and coking value; soft and medium pitch; hard pitch.

1. Introduction

Coal tar pitch is a mixture of high molecular weight poly cyclic aromatic compounds obtained as a residue from the distillation of coal tar. It is used as a binder in the production of anode for aluminium and electrode for graphite industries. Demand for quality pitch has gone up with the advancement of the aluminium and graphite industries. The quality of pitch is determined by its softening point, BI and QI content, Coking value (CV), β -resin, ash, density, viscosity *etc.* The binding properties of hard pitch are due to the presence of high molecular weight resins which determine its softening point and coking values. High carbon content and their miscibility with petroleum coke and pitch coke have made coal tar pitch unique in its applications.

The demand for hard pitch is about 88 000 t/year out of which aluminium industries account for 70 000 t. The remaining 18 000 t is consumed by graphite electrode and carbon paste manufactures. Each industry has its own requirements for the hard pitch for production of electrodes. Consequently, specifications of pitch is also different as shown in **Table 1**.

During 1993, the quality of tar at the Bokaro Steel Plant was inferior in terms of moisture, specific gravity, BI and QI *etc.* and hard pitch produced from it was not

matching the specifications of the customers. In view of this, a good quantity of soft pitch was converted into Pitch Creosote Mixture (PCM) and used as fuel in the rotary kiln.

Technology was developed jointly by RDCIS and BSL to use this inferior quality tar to produce hard pitch of suitable quality by blending, modifying operating process in the tar distillation and soft pitch processing unit.

2. Tar Quality

B. E. A. Thomas¹⁾ in a paper on electrode pitch, indicated that tars for the manufacture of electrode pitch

Table 1. Customer's specification for hard pitch.

Specification	Aluminium industries in India			Graphite industries in India	
Softening point (R & B) (SP) (°C)	109–113	> 105	95 + 5	95–103	102–107
Coking value (CV) (%)	> 58	> 52	50–53	55–56	> 55
BI (%)	30–37	> 27	> 30	28–29	> 30
QI (%)	10–12	5–12	> 10	9–11	12–15
β -resin (%)	> 25	> 20	> 20	20	> 17
Ash (%)	0.2	0.5	0.3	0.5	0.3

Table 2. Tar quality at BSL.

Month	Moisture (%)	Specific gravity	BI (%)	QI (%)
April 93	5.0	1.21	18.4	14.0
May 93	4.8	1.206	20.6	16.2
June 93	4.7	1.216	18.3	15.4
July 93	5.6	1.215	16.7	12.6
Aug. 93	6.4	1.21	17.2	11.9
Sept. 93	7.5	1.21	16.7	10.9
Oct. 93	10.1	1.203	16.8	11.4
Nov. 93	14.0	1.199	16.9	11.2
Dec. 93	5.4	1.204	17.3	11.7
Jan. 94	5.8	1.207	16.7	10.7
Feb. 94	5.6	1.208	17.4	10.6
March 94	5.1	1.210	16.0	10.7
April 94	4.4	1.209	17.0	11.4

should be aromatic rather paraffinic, and should contain high concentration of free carbon. To obtain tars of this nature, high free space temperature and light charging were advocated. These recommendations would be unacceptable to the coking industries.

The quality of tar in terms of specific gravity, moisture, viscosity and BI and QI varied from time to time at BSL and was very bad. This was mainly due to poor health of coke oven batteries and many unusual operating conditions like under charging of ovens, improper leveling of coal charge, high free space temperature, non-uniform coking period, non-cleaning of oven top equipment(stand pipes, goose neck, valve box and hydraulic main).

BSL tar was characterised by high moisture (4.4–14%), specific gravity (>1.2), viscosity, very high content of BI (15–17%) and QI (10–12%) compared to normal tar of 8–9% BI, and 4–5% QI content. The BSL tar quality on monthly basis is shown in **Table 2**.

3. Pitch Quality

Hard pitch produced from this inferior quality tar was having BI content of 35–40% and QI content of 20–22%. Therefore, this hard pitch was not matching the requirements of customers from aluminium and graphite industries.

4. Use of Hard Pitch as a Filler in Aluminium and Graphite Industry

Graphite electrodes are used for electric arc furnaces in the steel industry, carbon anodes for aluminium industries and speciality carbon for manufacture of bearings, piston rings *etc.* Manufacturing process consists of mixing of filler material (usually calcined petroleum coke) with pitch, forming the mix, and baking this green mix to 850–1300°C (electrodes 850°C, anodes 1300°C and speciality carbon 1300°C).

The amount of binder used varies from 15–50% depending upon the product. Electrodes require about 20%, anode 15% and speciality carbon 35–50%. The following properties are required for binder pitch at different stages of anode and electrode production:

- Good wettability and high binding during mixing

- Optimized weight loss characteristics during baking
- Good mechanical and electrical properties, low air and CO₂ burn during electrolysis.

The softening point of pitch should permit easy mixing with filler coke grit. It is necessary to have a SP of about 100°C (R & B). Insoluble benzene in pitch is termed as free carbon which contain high molecular weight (>1000) nuclei surrounded by lower molecular weight compounds. BI content in pitch should be in the range of 25–32%.

Quinolene as solvent dissolves about 60–70% of BI and insoluble part is termed as quinolene insoluble. QI content in pitch should be in the range of 10–15% and the presence of high molecular weight (>5000) in pitch helps in improving the mechanical properties of electrodes.²⁾

The soluble part (difference between BI and QI) is termed as β -resin, having a molecular weight between 1700–2100. This is a fusible mass and is a measure of binding strength of the pitch.

5. High Content of Coal Fines in Charge Coal

The effect of carbonization conditions on quality of tar produced has been dealt in detail by researchers from Marineau, France.³⁾ The content of –0.6 mm fraction in coal blend *versus* quality of crude tar with respect to BI and QI content is depicted in **Figs. 1** and **2**. It was observed that with increase in –0.6 mm fraction in coal blend, there is an increasing trend in BI and QI content of tar. It was further observed that when –0.6 mm fraction in coal blend increased to 43% for the month of May '93, as shown in **Figs. 1** and **2**, BI and QI value increased to maximum (BI-19.5% and QI-15.1%). To find out how much carry over and cracked BI and QI in tar was present, particle size of BI and QI residue of tar (isolated by filtration) was analysed on a micron photo sizer, Model SKC-2000. Results are shown in **Fig. 3** (cumulative graph) and **Fig. 4**.

For a good tar, the particle size of BI residue are less than 10 micron. Size fraction analysis as depicted in **Fig. 5** shows particles are coarser with more than 45% of particles in the range of 15–25 micron. This indicates substantial amount of carry over coal fines (<0.6 mm) present in tar which was responsible for high percentage of BI and QI content of BSL tar.

Crude tar samples collected from decanters, intermediate tank and storage tank were subjected to detailed characterisation. Tar samples collected were allowed to settle for 2–7 days before analysis. It was found that there were no appreciable change in BI and QI content in tar even after long settling time. This indicates that coal micro fines cannot be separated effectively by gravity settling in conventional decanter.

6. Approach

Various methods are available to alter pitch properties to make it suitable for electrode binder:

- Addition of aromatic oils with soft or medium pitch to change poly eutectic equilibrium to enable condensation of poly nucleic high molecular aromatic

Fig. 1. -0.6 mm fraction in coal blend and coal tar quality (BI).

Fig. 2. -0.6 mm fraction in coal blend and coal tar quality (QI).

Fig. 3. Particle size distribution for BI of coal tar (cumulative).

compounds.

- Treatment of tar before distillation.

7. Technology Development

Process development for the production of hard pitch was carried out in three phases:

- (1) Phase I:
 - Laboratory investigations with tar and soft pitch produced at BSL.
 - Optimizing the quantity of additive (anthracene oil)
 - Upgrading the quality of BSL tar by blending it with

Fig. 4. Particle size distribution for BI of coal tar.

Fig. 5. Tar blending facilities at BSL.

low BI and QI tar from other steel plants.

(2) Phase II:

- Development of process parameters by carrying out thermo-oxidative treatment of pitch and oil in various proportions in pilot scale.

(3) Phase III:

- Industrial trials to produce bulk quantity of pitch for customer's acceptability.
- Treatment of soft medium pitch after distillation.

8. Experimental

In the laboratory, various proportion of anthracene oil were added to soft pitch. The BI and QI and softening point of the mixture were determined to assess optimum quantity of anthracene oil required to produce the desired quality of hard pitch.

The pitch and oil mixture of 90 and 10 and 95 and 5% were subjected to thermo-oxidative treatment in pilot scale reactor at different air flow rate and aera-

Table 3. Pilot trial results.

Experiments	1	2	3	4	5	6
Pitch + oil (%)	90 + 10	90 + 10	90 + 10	95 + 5	95 + 5	100
SP of soft/medium pitch (°C)	79	78	80	82.5	80.5	81
SP of pitch + oil mixture (°C)	71	69.5	72	78	77	—
Air flow rate (Lit/H/Kg)	20	30	15	30	45	40
Duration (H)	4	3	5	4	4	3
Hard pitch quality						
SP (°C)	114	105	107	122	132	118
BI (%)	37.2	36.3	35.1	37.8	38.2	37.5
QI (%)	13.5	14.3	13.0	15.2	15.8	15.0
CV (%)	59.5	58.2	57.9	65.4	66.2	63.5

Table 4. Tar characteristics. Desired blended tar quality required for production of hard pitch for graphite industries. Moisture <4%, BI 11–13%, QI 6–7%.

Item	BSL	BSP	IISCO	VSP
Specific gravity (30°C)	1.21	1.18	1.202	1.176
Moisture (%)	8.0	3.5	4.6	2.0
BI (%)	16.3	7.2	10.8	5.3
QI (%)	10.7	3.8	6.8	2.5
Distillation residue (%)	69.9	59.2	62.7	57.8
SP of residue (°C)	83	76	85	91.5

tion period. Results of pilot plant experiments are presented in **Table 3**.

The second method tried was blending of low BI and QI tar from other steel plant with high Bland QI tar of BSL in various proportion. Low BI and QI tar from BSP (Bhilai), VSP (Vizag) and IISCO (Burnpur) were procured and blended with BSL tar in appropriate ratio to have desired final product (hard pitch). The blended tar was analysed for BI and QI content. The tar quality of BSP, VSP and IISCO are presented in **Table 4**.

9. Results and Discussion

It was observed from laboratory and pilot experiments that addition of anthracene oil does not help much when BI and QI content in tar is very high. It was also observed that with the increase in quantity of oil, the softening point of the mixture was reduced, thus requiring longer aeration period.

The blending of BSL tar with low BI and QI tar from other steel plant was the easiest solution for production of hard pitch to meet customer's requirement.

10. Commercial Trials

Commercial trials were conducted in the tar distillation

Table 5. Industrial trials results.

Trial No.	1	2	3
Blend ratio (BSL : BSP)	70 : 30	60 : 40	50 : 50
Analysis of feed tar			
Moisture (%)	1.8	2.0	2.5
BI (%)	13.6	12.7	12.0
QI (%)	8.4	7.7	7.2
Softening point soft/medium pitch charged into batch reactor	82	80	78
Operational parameters			
Temp. of straight run pitch charged into batch reactor (°C)	270	268	264
2nd stage tar flow rate (m ³ /h)	10	10.5	11
Temp. after 2nd stage evaporator (°C)	360	360	365
Air flow rate batch into reactor (m ³ /h)	550	600	650
Analysis of hard pitch produced			
Softening point of pitch (°C)	108	105	104
BI (%)	34.5	33.2	30.4
QI (%)	16.3	15.3	14.5
Coking value (CV) (%)	59	58.8	56.8
β -resin (%)	18.2	17.9	15.9

and pitch aeration section on the basis of laboratory and pilot scale investigation. Bulk quantity of hard pitch produced from commercial trials were sent to customers for evaluation. The quality of pitched produced conformed to customer's specification.

The following steps were taken for industrial trials on the basis of laboratory & pilot tests:

(1) Tar blending facility was installed near tar distillation section where low BI and QI tar from other steel plants were blended with high BI and QI tar produced by BSL for carrying out commercial trials. Tars from BSL and BSP were blended in appropriate quantity by pumping and mixing in a new storage tank to obtain optimum tar quality for distillation.

(2) Tapping of anthracene oil was stopped during the charging of straight run pitch into the batch reactor. This was to allow anthracene oil to mix with soft pitch and thereby reduce BI and QI content of soft-medium pitch in batch reactor for further processing *i.e.*, increase in softening point by aeration.

(3) Tar flow rate to 2nd stage evaporator increased to 10–12 m³/h, from 8 m³/h.

(4) 2nd stage tar temp. maintained at 360–365°C instead of 380°C.

(5) Optimum air flow rate during aeration was kept at 450 m³/h against about 100 m³/h kept earlier.

(6) Initial temperature of straight run pitch in batch reactor was kept around 270°C before starting of aeration (instead of about 250°C). The bulk quantity of hard pitch produced from commercial trial were sent to customer's site for evaluation. The quality of pitch produced conformed customer's specification. Results of commercial trials is presented in **Table 5**.

Industrial trials were jointly carried out by BSL and R & D Centre, SAIL with the above technological procedure. Hard pitch produced during these trials were tested at consumers sites and found suitable for actual use.

11. Conclusion

(1) Hard pitch produced from high BI and QI tar does not conform to customer's specifications.

(2) BI and QI content in hard pitch can be regulated by blending BSL tar with low BI and QI tar available from BSP, VSP and IISCO in appropriate ratio.

(3) Based on laboratory and pilot experiments, revised technological procedure suiting to this tar was formulated.

(4) Important process parameters such as tar blend ratio, 2nd stage tar temp. of 360–365°C and tar flow rate (10–12 m³/h), air flow rate (450 m³/h), initial temperature of soft pitch in reactor before aeration (around 270°C) and aeration period (8–10 h) were developed and established by these trials.

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Nomenclature

SAIL :	Steel Authority of India Limited
BSL :	Bokaro Steel Limited
BSP :	Bhilai Steel Plant
RSP :	Rourkela Steel Plant
IISCO :	Indian Iron & Steel Company
VSP :	Vizag Steel Plant
RDCIS :	Research & Development Centre for Iron & Steel
R & D :	Research & Development
RMP :	Refractory Material Plant
SP :	Softening point (°C)
R & B :	Ring & Ball
BI :	Benzene insoluble
QI :	Quinoline insoluble
β -resin :	Difference between BI & QI values
CV :	Coking value
PCM :	Pitch creosote mixture
Sp. Gr :	Specific gravity

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