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PERFORMANCE OF BINDER PITCHES WITH DECREASED QI-CONTENT IN ANODE MAKING
FORMATION - NATURE - PROPERITES AND SUBSTITUTION OF QUINOLINE INSOLUBLES

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ABSTRACT

Five different kinds of quinoline insolubles in binder pitches were investigated concerning their influence on the performance in anode making:

- primary QI
- secondary QI
- coal/coke breeze
- carbon black
- and ash

Experimental and commercial pitches were fully characterized using conventional anode binder specification tests and some additional tests including wetting behaviour, mesophase content and inorganic material. Bench-scale test anodes were produced using a prebaked type anode formulation with petroleum coke. Their chemical, electrical and mechanical properties were measured.

The results indicate that binder pitches with 6 - 8.5 % QI can provide optimum wetting properties and thus can be used to produce baked carbons of high performance.

INTRODUCTION

Coal tar for the production of binder pitch is a by-product of the manufacture of metallurgical coke. As tar quality is mainly influenced by the operation conditions in the coke ovens (temperature, coking time, hot charging, size and free space above the charge, temperature of the collecting main, and conditions of the ovens (1)), most tar processors receive crude tars of varying compositions. In order to generate binder pitches with a constant quality and with optimized properties, it is important to blend and treat the tars during binder production.

The quantity of the quinoline insolubles (QI) in the tar depends on several parameters, e.g. the amount of air present in the carbonization space due to leaking doors or through heating walls. The air causes local over-heating and incomplete combustion of gaseous products, which leads to an increased QI formation. In new cokeries the leaking of doors and walls is considerably reduced; that is the reason for a decreased QI level in "modern tars". Fig. I shows the age structure of the cokeries in the U.S., Japan and West-Germany and gives an explanation for the limited availability of high-QI tars.

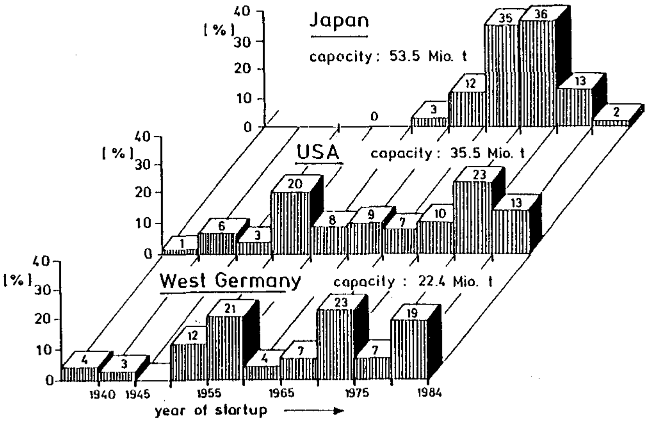

Figure I: Age structure of cokeries in the U.S., Japan and Western Europe

A possible way to generate artificial QI in order to meet pitch specifications with high-QI consists in thermal treatment of pitch. This procedure is still available at the request of the customer.

In recent years considerable research work has been carried out in this field showing that artificial QI like mesophases may result in inferior binder properties (2-3). In further studies it has been shown that binder pitches produced straight-run from low-QI tars are even superior to the high-QI pitches (4-7).

FORMATION AND NATURE OF QI

Primary QI is produced by thermal cracking and incomplete combustion of volatile components liberated during the coking process. It forms spheres which are less than 2 µm in size (Fig. I) and presents a C/H-ratio of more than 3.5.

Secondary QI is formed by polymerization of aromatic molecules in pitches at elevated temperatures. Its C/H-ratio is less than 3. Observed mesophase particles do not always account for all the secondary QI as parts of it may be soluble in quinoline. In contrast to the primary QI the mesophase particles are formed in the liquid and not in the gas phase. In the early stages of mesophase formation, the primary QI acts as nucleation sites thus increasing the rate of mesophase formation (8). Once the mesophase spherules have been formed, the primary QI particles act to restrict their growth by inhibiting their coalescence (9). Secondary QI is normally larger than primary QI particles.

Carry-Over is coke and heat-affected char particles which become entrained in the evolving tar vapours and are carried with them out of the coke oven. These particles vary greatly in size; they are mostly larger than primary QI (up to 300 µm).

Carbon Black or other dispersed solids present in pitch are often suggested for use as a supplement to increase the QI-content of the binder.

Ash originates from crude tar (respectively from the coal used and refractory material), corrosion products or added substances (like anti-corrosion additives).

Detection of Quinoline Insolubles in Pitches

Primary QI appears under the scanning electron microscope (SEM) as individual spheres. Sometimes in high-QI pitches they have agglomerated to form clusters, Fig. II. The carbon structure within a QI-sphere is onion-like, with graphitic layers in concentric shells parallel to the surface (10).

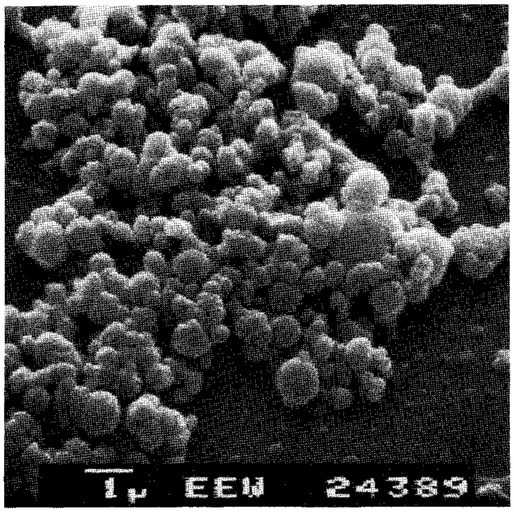

Figure II: Primary QI

The detection of secondary QI is possible under the SEM, Fig. III, as well as microscopically by observation under circularly polarized light. Microscopically the size and concentration of these spherules can be determined (11). This method is based upon the liquid crystal structure of the mesophase particles, making them easily visible under polarized light.

Carry-over particles can be detected because of their sharp contours and their great variation in size.

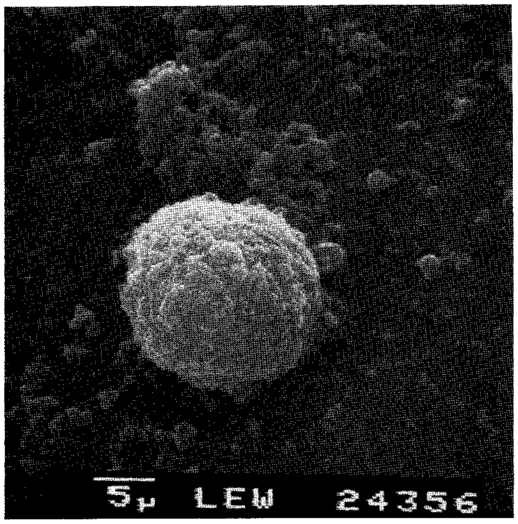

Figure III: Secondary QI
(Mesophase Particles with Primary QI on its Surface)

The degree of dispersion of carbon black in binder pitches mainly depends on the kind of grinding and intermixing applied for the carbon black. If large anisotropic areas from fine grain clusters of the added carbon black occur, the distribution is unsatisfactory. Only with considerable mechanical effort and expense it is possible to achieve an even distribution of the carbon black in the isotropic substrate which is necessary for good properties of the binder.

Normally, ash is not visible microscopically because of its size; under the SEM it is detectable concentrated on the surface of primary QI particles. Likewise carry-over contains a lot of ash.

The Influence of Solid Particles on the Properties of Pitch

As the coking value of solid particles in the binder is nearly 100 %, it is obvious that pitches containing high concentrations of QI will have higher coking values than low-QI pitches. In practical anode making less pitch is necessary when low-QI pitches are used (7). Thus the amount of volatiles released in the anode is reduced and the in situ coking value of the pitch is increased. By this effect higher baked densities of the anodes are achieved.

The viscosity of the binder pitch is influenced by its solid particles in two ways. First, the intended increase of QI causes a higher viscosity and softening point of the pitch. Secondly it has been found that the content of QI effects the slope of the viscosity-temperature curve. Low-QI pitches show a steeper slope, which means that they have a lower viscosity at working temperatures than high-QI pitches with the same softening point.

The Influence of Solid Particles in Pitch on the Binding of Coke

Solid particles in the pitch especially mesophase and carry-over reduce the binding capacity of the pitch, because

- they do not contribute to binding and thus reduce the effective binder content in the pitch
- they need binder for their own wetting.

Carry-over particles need even more pitch to be wetted, because of their irregular shape with large specific surface in contrast to mesophase particles with a spherical shape. Primary QI or carbon black also reduce the binding capacity of the pitch. As their contribution is necessary for optimized properties of the binder pitches, a limited amount, however, must be tolerated. Any excess of QI should be avoided as will be shown later in this paper.

EXPERIMENTAL

Binder Pitches

Six high-QI pitches of commercial origin were selected as reference materials; these were obtained from tar distillers and aluminium companies as typical examples of electrode binders.

Two samples of low-solid tars from modern coke-oven installations were obtained. These were distilled at atmospheric pressure in a 5-litre gas-heated still (Pitches 7 and 8). Two further pitches of medium-QI were taken from commercially available sources; they were produced by continuous vacuum distillation (Pitches 9 and 10).

Three pitches were produced on the laboratory scale from the low-solid tars, using modifications intended to raise the quinoline-insoluble contents to the levels required by typical aluminium company specification for anode binders.

Two of these pitches were made from the tar used to produce Pitch 7. These were produced by air-blowing a soft pitch (Pitch 11 had a higher softening point and was therefore fluxed back, Pitch 12 was obtained directly).

The third modified pitch was produced by dispersing carbon black in the low-solid tar used to produce Pitch 8. The tar was distilled until approximately 25 wt.% of distillate was obtained, then an amount of carbon black calculated to produce approximately 5wt.% in the finished pitch was dispersed at room temperature in the distillate, using a combination of high-speed high-shear stirring and ultrasonic agitation. Afterwards, this dispersion was mixed with pitch and distilled to the desired softening point (Pitch 13). The properties of the binder pitches are given in table I.

Petroleum coke aggregates

Three petroleum coke aggregates were obtained from two aluminium companies. They were typical of those in use at the time in producing prebaked-type anodes.

The electrodes produced from these cokes have identifiers prefixed A- for the first batch, AA- for the second one and AAA- for the third one.

All the coke blends used in producing test electrodes contained recycled crushed anode butts. The content of recycled butts material was approximately 25 mass% in all blends. The properties of the petroleum coke/butts blends are listed in table II.

Production of experimental test electrodes

Electrode pastes were produced by preheating the petroleum-coke aggregate in a 2-litre electrically-heated Z-blade mixer, then adding the required amount of the binder pitch as a coarse powder (-3.35 mm). Mixing was continued for 1 hour after the mixer had regained its set temperature 60K above the R&B softening point of the pitch.

The hot paste from the mixer was transferred to intermediate storage in an oven at 180 °C and was used to make eight cylindrical blocks 45 mm diam. and approximately 85 mm long using an electrically-heated double-action hydraulic press mould at 150 °C.

The green blocks were baked up to 1080 °C packed in petroleum-coke powder in saggers (bake-boxes), in batches of four.
The properties of the test electrodes are given in table III.

DISCUSSION

The bench scale test results are averages of single measurements ranging from 4 to 48, mostly 8 observations.

Performance of low- and medium-QI binders

The electrodes made with low-QI Pitch 7 had a greater green density than any from the high-QI commercial pitches. Although the mass loss on baking was at the higher end of the range for the high-QI commercial pitches, the density of the baked blocks and the disc apparent density were also higher than the highest values found with the prebaked-type high-QI commercial pitches. The volume change and coke pickup on baking were both within the range for the high-QI commercial pitches, as were the tensile strength, the CO_2 and air reactivities and their corresponding dust yields. Although the anode consumption rate was marginally above the range for the high-QI commercial pitches, the difference was not statistically significant. The principal advantage of the electrodes from Pitch 7 was their lower electrical resistivity than any from the high-QI commercial binders.

Considered overall, the electrodes from Pitch 7 performed as well as those from the high-QI commercial pitches and had the benefit of a lower electrical resistivity.

The electrodes made with Pitch 8 were superior to those made with the high-QI commercial pitches in green density, baking loss, baked block density, disc apparent density, electrical resistivity and anode consumption rate. Other properties fell within the ranges found for the high-QI commercial pitches.

The best results in this test were achieved with the two commercially available medium-QI pitches produced by continuous vacuum distillation and containing 6.3 and 8.5 % QI (Pitches 9 and 10). They showed by far the highest values in green, baked block and disc apparent density. In addition they were superior in electrical resistivity, CO_2-reactivity and permeability. The low optimum binder content in electrode production for these two pitches is noteworthy.

The overall performance of this group of electrodes can be considered to be rather better than those made with the high-QI commercial binders, and in the important areas of baking mass loss (i.e. carbon yield) and anode consumption rate it appears to have significant advantages.

Performance of experimental enhanced-QI-binders

The electrodes made using Pitch 9 were inferior in most respects to those from the high-QI commercial binders, mostly for reasons traceable to a low green density and a high baking mass loss. The underlying reason for the latter was undoubtedly the high content of distillable material in the pitch itself (12.1 mass%), at least partly due to the necessity of fluxing-back the hard primary air-blown-product.

Pitch 10 was made directly by air blowing without the use of fluxing oil; despite this, the product still had an abnormally high distillate yield at 360 ^{o} (7.3 mass%). The reasons for this are not clear, but it seems probable that the air-blowing process involves some molecular disproportionation in which the formation of high molecular weight QI material is accompanied by formation of lower boiling products.

With this pitch the baking loss was in the middle of the range found for electrodes made with the high-QI commercial pitches, as were most of the other physical properties apart from the air permeability which was higher, and the tensile strength, which was lower, neither difference being statistically significant.

Although the physical performance of Pitch 10 was unexceptional in the context of the high-QI commercial pitches, by comparison with its straight-run counterpart Pitch 7 it was inferior in most respects, mostly traceable to the initial low green density. The latter was almost certainly connected with the rheology of the electrode paste during mixing and forming. It has been observed elsewhere (12) that air-blown pitches have a low affinity for petroleum coke, and this appears to have been the case with Pitch 10.

The electrodes made with Pitch 11 (carbon black added) were superior to those made using the high-QI commercial prebaked-type binders in green density, baked block density, disc apparent density and electrical resistivity. They were marginally, but not significantly stronger, than the best of the electrodes from the high-QI commercial binders and had marginally, but not significantly, lower reactivities to air and CO_2.

The anode consumption rate of the electrodes from Pitch 11 was towards the lower end of the range for electrodes from the commercial binders.

Effect of carbon black on electrode properties

The basis for the use of carbon black as an additive to an electrode binder appears to be the observation that the primary QI present in high-temperature coke-oven tars and pitches has many of the characteristics of a thermal carbon black including its tendency to form chain-like aggregates of the ultimate particles (13).

Studies of the optical microscopic structure of the binder carbon formed during the baking of pitch-bound electrodes have suggested that the primary-QI present in the pitches promotes the formation of fine-mosaic texture in the carbon bridges by inhibiting the growth of mesopase particles (14,15). The fine-mosaic texture has been associated with superior strength when compared to the more highly-developed flow textures which are formed when the primary-QI is absent.

Formation of binder-coke bridges during carbonization

During baking the anode the binder pitch is transformed to binder coke. This particular property has been termed thermally induced "aromatic growth". Polycyclic aromatic hydrocarbons reach a very high coking value because of their structure. Their polymerizations to coke take place nearly exclusively by loss of hydrogen (16).

During production of the anodes the binder pitch has associated itself with the petroleum fines, but larger coke particles are not yet completely wetted. During carbonization the binder passes through a melting stage and becomes at higher temperatures fluid enough to wet the whole coke surface and even penetrate partly into the coke. All coke particles are coated with a pitch layer of at least 5 µm at 400 ^{o}C (Fig. IV). The distillation of pitch volatiles is nearly finished at 500 ^{o}C and polymerisation reactions start to prevail. Nevertheless, the pitch is still isotropic in nature. The pitch is converted at between 500 ^{o}C and 600 ^{o}C into an anisotropic green coke with mosaic structure. In practical anode baking this step will occur at lower temperatures due to the use of a reduced heating rate (0.2 K/min. instead of 1.0 K/min.) (17).

Figure IV: Anode piece calcined up to 400 ^{o}C

The anisotropy of binder coke relates to the mechanical strength of the anode. Formation of large flow domains will therefore decrease mechanical strength.

It is known that the QI-particles in binder pitches influence the magnitude of the flow-domains. Test specimen made from filtered pitch with a very little QI-content show very wide spreading flow domains. Evenly dispersed QI-particles such as primary QI or carbon black at a concentration of 6 to 8.5 % prevent the formation of these undesired flow domains. A higher QI-content has no further advantage in this respect, because most of the additional QI is located in clusters and this part of the QI cannot contribute to the reduction of flow domains anyhow. In addition, a higher pitch consumption for adequate wetting of the coke is required, when high-QI pitches are used.

CONCLUSION

Four straight-run pitches with QI contents between 2.9 and 8.5 % produced from low-solid tars were found to give bench-scale electrodes with physical properties at least as good as, and in most cases better than, those from the reference binders with QI-contents from 10.1 to 13.7 %. The optimum seems to be in the region of 6 to 8.5 %.

The key to the success of these low- and medium-QI binders appears to lie in the high green densities of the electrodes in which they were used, which more than offset any tendency to low coke yields or increased baking losses, and gave electrodes of high baked densities.

Examination of the correlations between the pitch properties and the electrode green and baked densities shows that the presence of mesophase has a marked negative effect on the green densitiy, and although the air-blown experimental binders contained no mesophase, they too gave electrodes of low green density. It has been demonstrated that heat-treated and air-blown pitches have higher viscosities in the 140 - 180 °C range, for a given softening point, than do their straight-run counterparts, and clearly the heat-treatment and air-blowing processes also affect their interaction with the petroleum coke grist in electrode pastes.

The results obtained here with carbon black additions in prebaked-type anode formulations do not show any very important improvements in the performance of the baked carbon.

Thus, in summary, it appears that pitches with decreased QI-levels produced from modern coke-oven tars can be used as binders to produce prebaked-type carbons having better properties or at least as good as those produced from current high-QI conventional binders. The low optimum binder content in electrode production especially for the vacuum distilled binder pitches with 6 to 8.5 % QI is a further advantage.

ACKNOWLEDGEMENT

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Table I Pitches: general properties

Pitch ref.	1	2	3	4	5	6	7	8	9	10	11	12	13
S. Pt. °C (R&B)	108.3	106.9	101.6	102.1	106.0	109.0	93.8	120.2	103.2	108.0	103.1	118.3	101.1
Q.I. mass%	13.7	11.2	13.2	11.3	10.2	10.1	3.1	2.9	6.3	8.5	13.0	14.9	7.5
T.I. mass%	34.5	32.6	33.7	32.4	34.0	36.4	23.5	27.4	26.5	29.7	35.1	38.1	25.7
C.V. mass%	59.6	57.3	58.2	58.5	56.4	54.5	54.9	59.0	54.4	56.1	51.8	57.1	54.9
Ash mass%	0.20	0.18	0.17	0.27	0.34	0.32	0.26	0.38	0.21	0.23	0.24	0.33	0.36
Dist. 360 °C mass%	2.3	4.3	4.6	4.7	4.4	3.7	4.8	1.6	1.1	0.9	12.1	7.3	2.2
Mesophase vol%	0.4	5.2	4.0	2.2	2.8	2.8	-	-	-	-	-	-	0.4
Largest sphere µm	18	22	48	12	36	46	-	-	-	-	-	-	6

S.Pt. = softening point Q.I. = Quinoline insol. content T.I. = Toluene insol. content

C.V. = Coking value (ISO)

Table II Properties of petroleum coke/butts blends

ELECTRODE BLEND REF.		A-	AA-	AAA-
Bulk density, g/cm^3		1.27	1.31	1.30
True density, g/cm^3		2.0227	2.0241	2.0230
Sieve analysis: cum. % undersize				
µm	4750	100.0	99.3	100.0
	2000	73.9	73.6	74.2
	500	45.4	45.5	44.9
	75	21.0	20.8	21.7

TABLE III Test electrode properties

ELECTRODE REF.	A 1	A 2	A 3	A 4	AA 5	AA 6	AA 7
Binder ref.	1	2	3	4	5	6	7
Binder content, wt%	17.44	17.19	17.73	17.60	16.30	16.19	16.56
Green density, g/cm^3	1.6281	1.6182	1.6222	1.6195	1.6355	1.6224	1.6630
Baking loss, mass%	5.2988	5.6207	5.6578	6.0292	5.1423	5.4304	5.9152
Block density, g/cm^3	1.5541	1.5353	1.5411	1.5418	1.5557	1.5581	1.5770
Volume change, %	-0.7938	-0.5298	-0.6899	-1.2932	-0.2746	-1.5273	-0.7852
Coke pick-up, mass%	0.5336	0.5033	0.2938	0.1517	0.0462	0.0713	0.4224
Disc. A.D., g/cm^3	1.5530	1.5294	1.5336	1.5278	1.5346	1.5434	1.5672
Disc. Ten. Str., MPa	5.8307	5.0810	5.3261	5.1551	4.9061	4.8775	5.5459
Core El. Res., μΩm	65.9550	67.8807	68.2645	65.4439	66.6367	65.5137	58.2711
Anode Cons. mass%	116.10	116.57	117.30	117.40	114.70	116.57	117.45
Disc CO_2 react. mass%	9.1625	10.3701	11.3062	9.4232	9.2688	8.4355	8.8207
Dust loss, mass%	2.7990	5.3229	7.2726	3.1557	4.5970	3.7743	2.7200
Disc. air react. mass%	5.4441	7.2132	5.6139	6.3289	4.7646	3.8356	4.4688
Dust loss, mass%	0.3497	0.1772	0.4514	0.4468	0.3516	0.2552	0.2501
Permeability μm^2	ND	ND	ND	0.1605	0.1609	0.1557	0.1200

ELECTRODE REF.	AA 8	AAA 9	AAA 10	AA 11	AA 12	AA 13
Binder ref.	8	9	10	11	12+	13
Binder content, wt%	15.06	14.25	14.50	16.50	15.86	16.52
Green density, g/cm^3	1.6620	1.6710	1.6740	1.6353	1.6299	1.6619
Baking loss, mass%	4.4419	3.9300	4.1100	6.3477	5.4919	5.7164
Block density, g/cm^3	1.6001	1.6070	1.6090	1.5353	1.5500	1.5835
Volume change, %	-0.7448	-0.6500	-0.6800	-0.2450	-0.6172	-1.0452
Coke pick-up, mass%	0.0341	ND	ND	0.0645	0.0495	0.1238
Disc. A.D., g/cm^3	1.5830	1.5880	1.5930	1.5185	1.5312	1.5729
Disc. Ten. Str., MPa	5.6672	5.9200	6.1300	4.2457	4.5120	6.0479
Core El. Res., μΩm	61.5061	60.4000	58.9000	66.1400	67.2446	59.8061
Anode Cons. mass%	112.40	ND	ND	117.73	114.13	115.15
Disc CO_2 react. mass%	7.8790	7.5300	7.4800	11.8827	9.0078	8.0410
Dust loss, mass%	1.2821	1.3100	1.2800	8.2420	2.5829	1.2089
Disc. air react. mass%	6.8287	ND	ND	6.1419	3.9482	3.7869
Dust loss, mass%	0.3044	ND	ND	0.2758	0.2530	0.1943
Permeability μm^2	0.0862	0.0930	0.0880	0.2262	0.1749	0.1296

ND = Not determined

+Baking furnace failure on first batch. Baked properties given for second batch only (4 observations).