PETROLEUM RESIDUALS IN PREBAKED CARBON ANODE BINDERS

By

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INTRODUCTION

In the Hall-Heroult Process for producing aluminum, alumina dissolved in molten cryolite at 950-1000°C is electrolyzed using a carbon lined cell as cathode and baked carbon as anode. Anodes are made by mixing about 18 per cent binder with 82 per cent carefully sized calcined petroleum coke and molding a green block, which is subsequently baked at 1100° in an inert atmosphere to coke the binder.

During electrolysis the anode in slowly consumed. Carbon consumption is caused by: (1) combination of carbon with the oxygen released at the anode, (2) further combination of carbon with CO_2 initially formed, (3) air-burning of the exposed top of the anode, and (4) disintegration caused by particles of petroleum coke falling into the bath if the binder coke is more reactive than the petroleum coke. All but the first are strongly affected by the reactivity of the carbon anode, and this in turn is dependent on the quality of the coke formed by the binder.

Numerous tests have been proposed for characterizing binders. They have been reviewed comprehensively by Thomas[3] and somewhat more critically by Weiler[4]. It is generally agreed that the binder should meet a softening point requirement for ease of processing, must have a low ash content to prevent contamination of the bath and also to avoid catalyzing carbon reactivity, and should be low in sulfur because of corrosion problems. In addition, high aromaticity[1] is desirable to form a less reactive anode with good electrical conductivity. Coke-oven pitch derived from coal is very aromatic and meets all these requirements. It is the binder used almost exclusively in the United States. We have now found that certain less-aromatic materials, such as those derived from petroleum, can be blended with coke-oven pitch to produce anodes equivalent in all significant properties to conventional anodes.

ANALYTICAL PROCEDURES

Softening Point

Cube-in-air method. Barrett Test No. D-7, Allied Chemical and Dye Corporation, New York, New York.

Reactivity

Sodium sulfate reactivity is the loss in weight on immersing a 1-in. cylinder of carbon 0.5-in. long for 30 minutes in sodium sulphate at 980°C. Carbon is oxidized by molten sodium sulphate[2]. A reference carbon containing a standard binder is always run with this test for comparison. Both results are reported here since for some of the earlier tests the procedure was modified slightly.

Infrared Index of Aromaticity

This is taken as the ratio of the aliphatic transmittance at 3.4 microns

Infrared Index of Aromaticity

divided by the aromatic transmittance at 3.3 microns as previously described[1].

Miscibility Test

This test measures the compatibility of a binder with coke-oven tar. A 1:1 mixture of the binder under test and coke-oven tar is heated about 30 degrees above the softening point. A small droplet is transferred to a warm glass microscope slide on a hot plate and covered with a cover glass. While still warm, slight pressure is applied to the cover glass to reduce the film thickness so that it will transmit light. When viewed under the microscope at 200X, absence of flocculation of the C-I particles normally present in coke-oven pitch indicates compatibility of the binder.

RESULTS AND DISCUSSION

A typical analysis of coke-oven pitch binder for prebaked electrodes is given in Table I. The softening point corresponds to about 215-233°F ring-and-ball.

TABLE I

TYPICAL PROPERTIES OF COKE-OVEN PITCH BINDERS FOR PREBAKED ANODES

Softening point, cube-in air	105-115
Sulfur, %	0.5
Ash, %	0.1
Infrared index	1.3

For carbon anodes made with unblended binders, the reactivity increased with decreasing aromaticity of the binder as measured by infrared index (Figure I). On the basis of infrared index binders may be divided somewhat arbitrarily into three aromaticity classes: high (>1.2), intermediate (0.6 to 1.2) and low (<0.6).

High Aromaticity Binders

Coke-oven pitch is about the only member of this class. In prebaked anodes almost any high-temperature, coke-oven pitch can produce a good anode.

Intermediate Aromaticity Binders

Pitches derived from vertical retort tars or oil-gas tar, and petroleum residuals from high temperature cracking processes fall in this class.

Low Aromaticity Binders

Among these are pitches derived from low-temperature coal tar, solvent extracts of petroleum and most petroleum residuals.

In general low and intermediate aromaticity binders do not produce good anodes and are not used alone in carbon anodes. In the United States a very minor amount of oil-gas pitch is used in 50:50 blends with coke-oven pitch.

Low Aromaticity Binders

In a search for low cost binders derived from petroleum, several residuals were found which unexpectedly produced good anodes in blends. Typical laboratory results are presented in Table II, and similar good results have been obtained in plant operation for several of these binders.

All intermediate aromaticity binders tested produced good anodes when blended with coke-oven pitch. These results were not unexpected since blends of oil-gas pitch have been used for some time in anodes. Recently residuals produced in petroleum processing by high-temperature cracking have become available. Those having intermediate aromaticity (A and B in Table II) should find application blended in anode binders. None of the petroleum residuals tested had aromaticities as high as coke-oven pitches.

Certain low aromaticity binders when blended with coke-oven pitch produced good binders. These included a petroleum residual (C - Table II) produced by propane deasphalting of an Ordovician crude and a pitch (D) derived from low-temperature lignite tar. Other low aromaticity binders, such as air-blown asphalt (E in Table II), produced poor binders. The only laboratory test which differentiated among these binders was the miscibility test. Those blends in which the C-I particles were flocculated produced poor binders (E and F in Figure 2). If the C-I particles remained uniformly dispersed (A and C in Figure 2) the blend produced good anodes.

While some of these binders did produce good anodes, their true coking values were lower than that of coke-oven pitch (Table II). This did not seem to affect their utility, but their economic value was lowered since less carbon would be available for reaction with oxygen produced at the anode in smelting cells.

CONCLUSION

High aromaticity binders can be used alone to produce good anodes. Intermediate aromaticity binders blended with coke-oven pitch produced good anodes. In blends low aromaticity binders which were miscible with coke-oven pitch produced good anodes.

REFERENCES

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2. Fotiev, A.A., Zh. Prikl. Khim. 35, 2402-9 (1962)

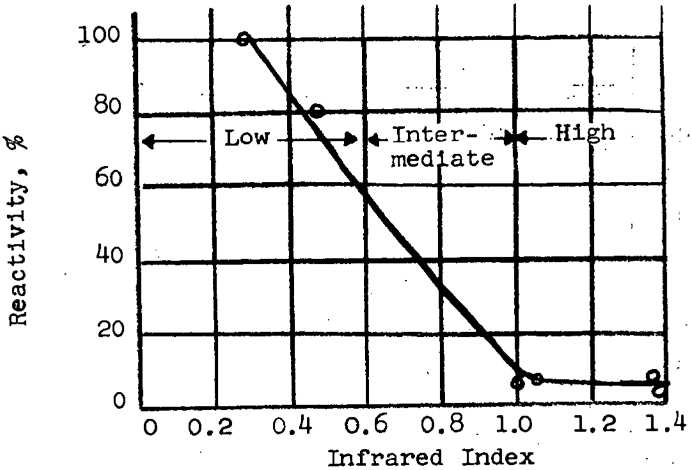
3. Thomas, B.E.A., Gas World, Coking Supplement 51-66 (April 2, 1960)

4. Weiler, J.F., "Chemistry of Coal Utilization", Lowry, H.H. - ed. Supplementary volume, John Wiley & Sons, Inc., New York, 1963 P. 627

TABLE II

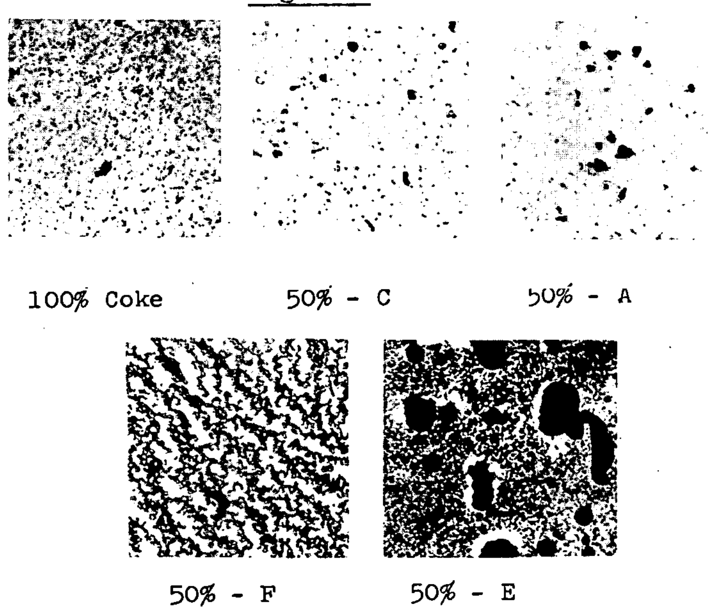
BINDER BLENDS IN LABORATORY PREBAKED ANODES

Binder	Source	IR Index	Coke-Oven Pitch in Blend, %	Binder %	Actual Coking Value, %	Anode Properties Resistivity ohm-in.	Anode Properties Reactivity %
A	Pet. therm. Process	1.07	50	18.5	52.7	0.0024	11.9
Reference	Coke-oven pitch		100	17.5	64.2	0.0023	22.6
B	Pet. therm. Process	0.78	60	17.5	55.9	0.0021	33.6
Reference	Coke-oven pitch		100	17.5	68.8	0.0022	57.0
C	Pet. propane deasphalt.	0.3	50	17.5	49.7	0.0023	30.1
Reference	Coke-oven pitch		100	17.5	63.4	0.0026	46.8
D	Lig., low-temp. carb.	0.14	60	18.5	-	0.0026	6.7
Reference	Coke-oven pitch	1.36	100	18.5	-	0.0025	5.6
E	Pet. air-blown	0.11	50	18.5	-	0.0035	9.3
Reference	Coke-oven pitch	1.32	100	18.5	-	0.0022	4.5



Reactivity of
Laboratory Prebaked Anodes

Figure 1



Miscibility Test Micrographs of Coke Oven
Pitch Blends (Transmitted Light, 200X)

Figure 2