

COAL TAR AND PETROLEUM PITCHES AS BINDERS  
FOR PREBAKED ELECTRODES

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INTRODUCTION

It has been shown that improved binders for Soderberg electrodes can be made by incorporating a rubber reinforcing grade of carbon black in low grade coal tar pitch or a residue from catalytic cracking of petroleum. At the concentration used (1-1.5% of the paste) carbon blacks cannot function merely as a partial replacement for coke fines. The high surface area, small particle size reinforcing blacks improve the homogeneity and mechanical stability of the binder-coke mixture by preventing the separation of oily components at high temperatures and apparently have a catalytic effect on polymerization and condensation reactions associated with coking of the binder.

A cracked petroleum pitch containing carbon black has also been compared to coal tar pitch in a prebaked electrode formulation. In the manufacture of prebaked electrodes, sized calcined coke and/or anthracite aggregate is mixed with 20 to 25% of coal tar pitch at 100-150°C using a hydraulic ram press. A small amount of paraffinic mineral oil is added to the mix to act as a lubricant during extrusion. Extruded electrodes are cooled in a water bath, then packed in sand and baked in a gas-fired pit furnace. The temperature in the furnace is increased gradually over a period of about 30 days to a maximum of 950-1000°C. After baking, the electrodes are cooled, repacked in calcined coke, and graphitized by heating to 1500-3000°C.

The coking characteristics needed in a binder for prebaked electrodes are generally similar to those for Soderberg paste, though lower paste fluidity is adequate for prebaked electrodes: while the paste must be fluid enough to permit forming by extrusion, it is not necessary or desirable that it flow under its own weight.

EXPERIMENTAL

The properties of a coal tar pitch (K) suitable for the manufacture of prebaked electrodes are given in Table 1 along with those of three petroleum binders. Binder H was prepared by dispersing 2.5% of fluffy (unpelletized) ISAF black in the pitch by mechanical stirring. Pitches G and J were made via a colloidal dispersion of commercial pelletized SRF carbon black in an aromatic oil, followed by distillation in vacuo, as previously described.

Thermogravimetric Analyses

Many electrode manufacturers use thermogravimetric analysis (TGA) of the binder to establish the temperature cycle for baking electrodes so that the rate of evolution of hydrocarbon vapours can be controlled. Too rapid emission of gases may cause electrodes to crack during the baking operation. Since the vapours are burned in the furnace

pit and contribute heat to the baking process, a moderate rate of volatilization is required to provide good temperature control. According to a common laboratory procedure, a weighed sample of pitch is placed on a balance pan enclosed in a furnace, the temperature of which is increased to 650°C over a period of 10 hours under nitrogen, and the loss in weight is determined at several temperatures.

The results of coking tests carried out by this procedure (TGA No. 1) on coal tar pitch K and petroleum binder H are shown in Figure 1. Although the initial temperature for evolution of volatiles was about 100°C higher for H than for K, the maximum rate of volatilization (slope of the linear part of the thermogram) of H was greater, and above 600°C it lost weight at a faster rate than K. Rapid loss in weight and a low carbon residue by TGA are generally considered to indicate a tendency to form a porous electrode. However, some doubt remained about the validity of this accelerated TGA test; as noted above, when electrodes are baked commercially, the temperature is raised much more slowly.

A TGA test (No. 2) was carried out at a much lower heating rate. Samples of binder in crucibles were heated for 22 hours in a nitrogen atmosphere at each of seven temperatures from 250 to 800°C, total heating time: 154 hours. After each period, the crucibles were removed from the furnace, cooled in a desiccator, and weighed. The results (Figure 2) differed markedly from those obtained by rapid heating. The coal tar pitch still began to vaporize at a lower temperature than the petroleum pitches G and H, but the maximum rate of volatilization was about the same for all. The different shape of the initial part of the curve for pitch K was shown previously by vacuum distillation analysis to be due to its higher content of non-coke forming light ends as compared to cracked petroleum pitch binders<sup>(1)</sup>.

After slow heating to 800°C, the weight of residue was virtually the same for all pitches. The amount of coke was 69-72% of the binder, as compared to 52-60% by the conventional isothermal coking value test (2.5 hours at 550°C) and the rapid heating TGA method. This is in agreement with Charette and Girolami<sup>(2)</sup> and Martin and Nelson<sup>(3)</sup>, who observed that the amount of coke from some coal tar pitches varied inversely as the rate of heating, since slow heating favours condensation and polymerization over cracking and volatilization. Heating rate has a greater effect on cracked petroleum pitch containing carbon black than on coal tar pitch: the difference in the amount of coke from slow and fast heating TGA tests was larger for H (72 vs 52%) than for K (69 vs 60%). This can undoubtedly be explained by the higher proportion of distillable coke forming components in a cracked petroleum residuum as determined by vacuum distillation and analysis of narrow cuts<sup>(1)</sup>.

A third series of TGA tests were carried out to determine the effect of the presence of petroleum coke aggregate. Girolami<sup>(4)</sup> reported that coal tar pitch has a higher apparent coking value when heated in the presence of calcined coke particles than when heated alone. In our test, (TGA No. 3) mixtures containing 23% binder and 77% calcined coke flour\* were heated for 22 hours at each of six temperatures

\* Coke I, Figure 4

between 300 and 800°C. As indicated in the next section, the proportions of binder and coke used were about optimum for prebaked electrodes made from this aggregate.

The results of the tests, shown in Figure 3, were quite different from those observed for the binders alone at the same heating rate. The initial evolution of volatiles from all of the mixtures occurred at the same temperature (300°C) but at about double the rate observed for the pure binders at 300-450°C, indicating interaction between the pitch and coke. At the same final temperature (800°C) the weight loss was higher than when the binders were heated alone, a result in disagreement with the observations of Girolami, and of Martin and Nelson above. The cracked pitch H containing only 2.5% carbon black had an extremely low effective coking value (29), whereas the one with 5% carbon black and the coal tar pitch both had about 50. Conclusions are that the additional 2.5% carbon black in G is of benefit during the baking procedure and this is borne out by the electrode test data presented in the following section.

#### Evaluation of Test Electrodes

The three petroleum binders and coal tar pitch, inspections of which are given in Table 1, were compared in several prebaked electrode formulations containing 21 to 27% binder. Two calcined coke aggregates were used, with particle size distributions as shown in Figure 4. About 2% extrusion oil based on the coke was added to the mixture. The coke and binder were stirred in a sigma bladed mixer at about 160°C and molded at 130°C under a pressure of 5,000 psig. After cooling to 95°C, the samples were removed from the molds, measured and weighed. The binders all gave similar molded green mix densities. The green electrodes were packed in calcined coke in stainless steel molds for baking, which was carried out in a 48 hour controlled temperature cycle. The electrodes were held at the maximum temperature of 1000°C for 2 hours. After cooling in the furnace, they were removed from the molds, brushed free of coke scale, measured and weighed, then machined to obtain specimens 2.5 inches in diameter and 3 inches long which were evaluated for density, electrical resistivity, and compressive strength. Experimental data for the mixes containing the optimum amount of binder (22-23 wt %) are summarized in Tables 2 and 3. The average loss of volatiles from cracked pitch (5.0% SRF black) using the two coke aggregates was the same as for the coal tar pitch (33-34%), but the others containing only 2.5% black lost 37 and 40% in weight respectively.

Table 4 gives a comparison of effective coking values obtained by five procedures: the isothermal coking test, three laboratory TGA tests and during baking of electrodes. The isothermal test, which agrees with the Norske method<sup>(2)</sup>, and the rapid heating TGA procedure (No. 1) both gave less coke than when electrodes were baked. This result confirms results reported by Martin and Nelson<sup>(3)</sup>. The slow heating TGA procedure (No. 2) on the binders alone gave a coke yield somewhat higher than that found in the baking tests. However, TGA test No. 3 on the binder/coke mixture produced substantially less coke than by electrode baking, a result that is not susceptible to a plausible explanation.

It appears that thermogravimetric analysis of the binder alone at a very slow heating rate can be used to predict the approximate yield of coke from coal tar pitch binders and possibly from cracked petroleum binders containing the optimum amount (about 5%) of carbon black. However, it must be concluded that in other cases a reliable indication of performance is obtainable only by preparing and baking test electrodes.

Figure 5 shows the density of baked test electrodes as a function of the amount of coked binder (coke residue, wt %, x binder content). Each curve has a maximum corresponding to the optimum amount of coked binder. An electrode made using pitch G with the optimum carbon black content had a maximum baked electrode density at least as high as coal tar pitch binder.

As expected, the compressive strength of baked test electrodes varied directly with electrode density, and for the same coke aggregate the relationship is independent of the origin of composition of the binder (Figure 6). The indicated higher average strength of electrodes made from coke I may be due to the denser grading of this aggregate in the coarse fractions.

The electrical resistivity of baked electrodes decreased with increasing electrode density as shown in Figure 7. Because coke II is more densely graded in the fine fractions, electrodes made from this aggregate had lower electrical resistivity than those made from coke I, especially at low electrode densities.

#### ACKNOWLEDGEMENT

The assistance of W. D. Horley in the laboratory evaluations and of Esso Research Laboratories, Baton Rouge, Louisiana, personnel in baking and testing of electrodes is gratefully acknowledged.

#### LITERATURE CITED

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- (3) Martin, S. W. and Nelson, H. W., Ind. Eng. Chem. 1958 50, 33
- (4) Girolami, L., "Effect of Aggregate on the Coking of Binder in Petroleum Coke-Pitch Mixtures;" paper presented at symposium on Non-Fuel Uses of Coal, American Chemical Society, Cincinnati, Ohio, meeting, January 13-18, 1963.

**COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR PREBAKED ELECTRODES**

**PROPERTIES OF BINDERS FOR PREBAKED ELECTRODES**

COMPOSITION WT %	Coal Tar		Cracked Petroleum Pitch	
	Pitch K	G	H	J
VACUUM REDUCED				
CAT CRACKING RESIDUE	85	97.5	97.5	
SRF CARBON BLACK	5		2.5	
ISAF CARBON BLACK				2.5
<b>PROPERTIES</b>				
SOFTENING POINT (CA) °C	100	97	102	100
DENSITY AT 15°C g/cm <sup>3</sup>	1.31	1.23	1.22	1.22
CONING VALUE, WT %	58	52	54	53
BENZENE INSOLUBLE, WT %	31	8	3.5	3.5
DUNDLIN INSOLUBLE, WT %	8	5	2.5	2.5
C/H (ATOMIC) RATIO	1.7	1.3	1.3	1.3

Table 1

**THERMOGRAVIMETRIC ANALYSES OF BINDERS FOR PREBAKED ELECTRODES BY TGA PROCEDURE NO.1**

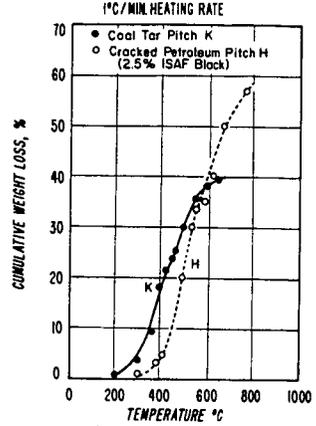


Figure 1

**THERMOGRAVIMETRIC ANALYSES OF BINDERS FOR PREBAKED ELECTRODES BY TGA PROCEDURE NO.2**

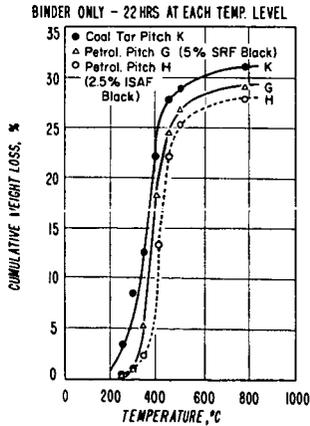


Figure 2

**THERMOGRAVIMETRIC ANALYSES OF BINDERS FOR PREBAKED ELECTRODES BY TGA PROCEDURE NO.3**

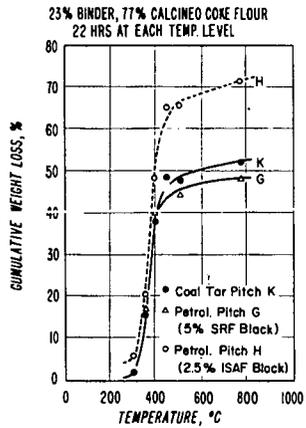


Figure 3

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR PREBAKED ELECTRODES

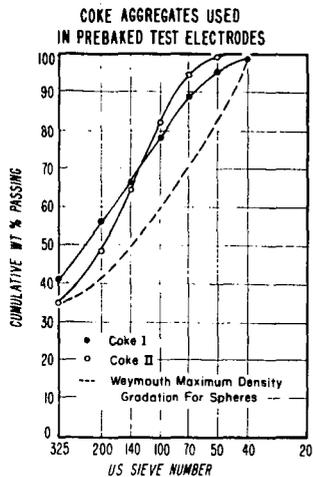


Figure 4

PERFORMANCE OF BINDERS IN PREBAKED ELECTRODES

BINDER	Coal Tar Pitch	Cracked Petroleum Pitch		
		K	H	J
CARBON BLACK IN BINDER	-	5%SRF	25%ISAF	25%SRF
BINDER CONTENT, WT %	23.0	23.0	23.0	23.0
<b>BAKED ELECTRODES</b>				
DENSITY, g/cm <sup>3</sup>	1.49	1.50	1.45	1.43
ELECTRICAL RESISTIVITY, 10 <sup>3</sup> ohm cm	1.09	1.08	1.13	1.16
COMPRESSIVE STRENGTH, kg/cm <sup>2</sup>	508	543	329	326

\*OPTIMUM 2, PARAFFINIC EXTRUSION OIL ADDED IN ADDITION TO BINDER

Table 2

PERFORMANCE OF BINDERS IN PREBAKED ELECTRODES

BINDERS	Coal Tar Pitch	Cracked Petroleum Pitch		
		K	H	J
CARBON BLACK IN BINDER	-	5%SRF	25%ISAF	25%SRF
BINDER CONTENT, WT %	23.0	23.0	22.0	22.0
<b>BAKED ELECTRODES</b>				
DENSITY, g/cm <sup>3</sup>	1.50	1.46	1.46	1.45
ELECTRICAL RESISTIVITY, 10 <sup>3</sup> ohm cm	1.06	1.08	1.08	1.15
COMPRESSIVE STRENGTH, kg/cm <sup>2</sup>	467	357	378	221

\*OPTIMUM 2, PARAFFINIC EXTRUSION OIL ADDED IN ADDITION TO BINDER

Table 3

EFFECTIVE COKING VALUE OF BINDER PITCHES

BINDER	Coal Tar Pitch	Cracked Petroleum Pitch		
		K	H	J
CARBON BLACK IN BINDER	-	5%SRF	25%ISAF	25%SRF
<b>COKING PROCEDURE</b>				
ISOTHERMAL, 25HR AT 550°C	-	58	52	54
TGA 1 - 10 HR TO 850°C (binder only)	-	60	-	52
TGA 2 - 154HR TO 800°C (binder only)	-	69	71	71
TGA 3 - 132HR TO 800°C (23 binder, 77% coke)	-	48	51	129
ELECTRODE BAKING 48HR TO 1000°C (23 binder, 77% coke)	-	67	66	63

Table 4

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR PREBAKED ELECTRODES

RELATIONSHIP BETWEEN BAKED ELECTRODE DENSITY & COKED BINDER CONTENT

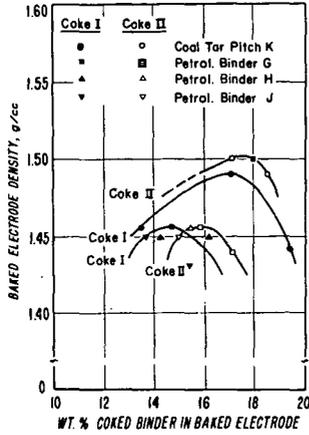


Figure 5

RELATIONSHIP BETWEEN COMPRESSIVE STRENGTH & DENSITY OF BAKED TEST ELECTRODES

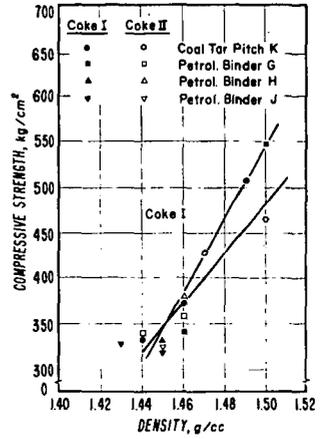


Figure 6

RELATIONSHIP BETWEEN ELECTRICAL RESISTIVITY & DENSITY OF BAKED TEST ELECTRODES

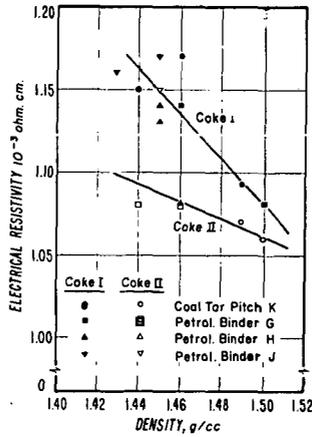


Figure 7