USE OF METAL CHLORIDES AS COKING ADDITIVES TO PITCH

Richard L. Shao[1], Irwin C. Lewis[2]
[1]*GrafTech International Ltd., 12900 Snow Road, Parma, OH 44130, USA*
[2]*Consultant*

Corresponding author e-mail address: Richard.Shao@graftech.com

Introduction

Graphite products, such as electrodes for steel production are manufactured using calcined coke filler and coal tar pitch binder as precursor materials. The pitch in a molten state is admixed with coke particles and then extruded to form a green artifact. The product is then baked to about 800°C to convert the pitch component to an infusible carbon state followed by heat treatment to about 3000°C to effect graphitization. It is important that the pitch maintains its fluidity during the mixing and forming stages. Additionally, it is desirable to maximize the binder carbon yield after baking so as to achieve optimal product density and strength. In practice, commercial coal tar pitches are prepared with a specific softening point defined to achieve the appropriate rheology at mixing and forming temperatures. The final binder carbon yield is fixed by the thermal distillation procedure used in pitch production.

There is extensive literature on the use of chemical additives to increase the carbon yield of binder pitches [1]. To be effective, the additive should have a minimal effect on the rheology of the pitch during the initial mixing and forming steps but react with the pitch during the baking stage to increase pitch carbon yield. Reagents that have been used include: sulfur [2], aromatic nitro compounds [3], quinones [4], and various metal halides [5].

In this study, we have investigated the use of several metal chlorides including $SnCl_2{\bullet}2H_2O$, $FeCl_3{\bullet}6H_2O$, and $ZnCl_2$, as well as sulfur and dinitrobenzoic acid as additives to coal tar pitch. In addition to determining the pitch/additive carbon yields, the effects of the reagents on pitch reactivity were assessed from viscosity measurements at mixing temperatures. The reagent $SnCl_2{\bullet}2H_2O$ was selected for use in fabrication of 150mm-diameter graphite electrodes in order to evaluate the relevance of binder carbon yield to final graphite properties.

Experimental

<u>Carbon Yields and Reactivity:</u> Reagent grade $SnCl_2{\bullet}2H_2O$, $ZnCl_2$, $FeCl_3{\bullet}6H_2O$ and 3,5-dinitrobenzoic acid were blended at the 3wt% level, and sulfur at the 5wt% level with a

110°C softening point coal tar pitch. The coking yields of the blends were then determined using the Modified Conradson Carbon (MCC) procedure.

Portions of each blend were then heated at 160°C in a viscosity measuring apparatus in order to monitor the pitch/additive reactivity as a function of time. More detailed studies were carried out with the $SnCl_2 \bullet 2H_2O$ additive including baking simulation and reaction with the aromatic hydrocarbon anthracene.

Preparation of 150mm-Diameter Graphite Electrodes: 150mm-diameter electrodes were fabricated at GrafTech's pilot-plant facility using a 3wt% $SnCl_2 \bullet 2H_2O$/pitch blend. The electrode properties were followed from the green stage through graphite.

Results

1. Carbon Yields and Reactivity

Summarized in Table I are the results for the carbon yield and viscosity measurements made for the pitch/additive blends. The viscosities represent the initial and final values measured after 2 hours of heating at 160°C. We were unable to obtain stable viscosity data for the $FeCl_3 \bullet 6H_2O$ blend.

Table I. Effect of Additives on Carbon Yield and Viscosity of Coal Tar Pitch

Additive	wt%	MCC (%)	Initial Viscosity (poises)	Final Viscosity (poises)
None	0	59.6	9.5	15.1
$ZnCl_2$	3	69.2	38.0	47.3
$SnCl_2 \bullet 2H_2O$	3	69.3	17.3	18.0
$FeCl_3 \bullet 6H_2O$	3	64.2	n/m	n/m
Sulfur	5	63.0	22	21
3,5-Dinitrobenzoic acid	3	62.6	16.0	38.0

From the results in Table I, it was apparent that the $SnCl_2 \bullet 2H_2O$ additive had the most favorable combination of effects for increasing carbon yield with a minimal effect on pitch viscosity at the 160°C mixing temperature.

2. Addition Levels for $SnCl_2 \bullet 2H_2O$

In order to determine the optimum addition level for the $SnCl_2 \bullet 2H_2O$, the carbon yields were measured for blends containing from1-5wt% with pitch. The results summarized in Table II show that the addition of as little as 1.5wt% has a substantial effect on the carbon yield of coal tar binder pitch.

Table II. Effect of $SnCl_2 \bullet 2H_2O$ Addition on the MCC of Coal Tar Pitch

Addition Level (wt%)	MCC (%)	MCC (pitch only)* (%)
0	59.1	59.1
1.5	67.4	66.6
2.0	68.1	67.0
3.0	69.3	67.7
5.0	69.6	67.0

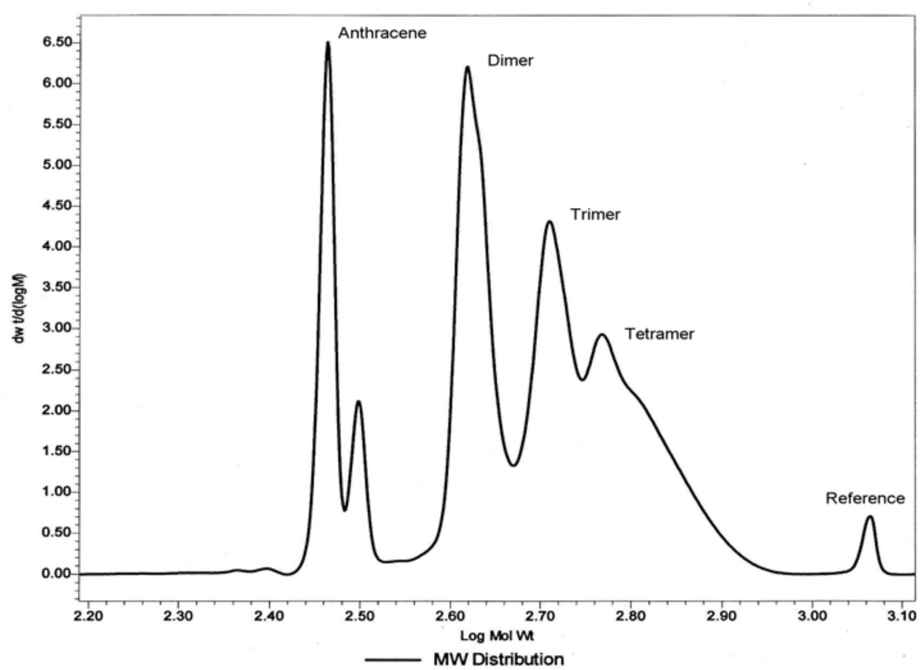
* Corrected assuming 100% retention of Sn.

3. Reaction Studies With $SnCl_2 \bullet 2H_2O$

In an attempt to clarify some of the chemistry involved with $SnCl_2 \bullet 2H_2O$ as a coking catalyst, we performed some exploratory laboratory studies with the model aromatic hydrocarbon anthracene.

A mixture of anthracene and 3wt% of $SnCl_2 \bullet 2H_2O$ was heat treated at 260°C for 16 hours. We obtained a 78% yield of a pitch-like material that melted at about 100°C and transformed to a fine-domained mesophase when heated at 450°C. A gel permeation chromatogram (GPC) for the initial "pitch" product is shown in Figure 1. In addition to a peak for unreacted anthracene, peaks corresponding to anthracene oligomers (dimers, trimers and tetramers) can be identified in the chromatogram. An NMR analysis of the "pitch" showed the presence of aliphatic hydrogens attributed to hydroaromatics and methyl and ethyl side chains.

Figure 1. Gel Permeation Chromatogram for "Pitch" from Anthracene and $SnCl_2 \bullet 2H_2O$ Mixture



4. Pitch/$SnCl_2 \bullet 2H_2O$ Baking Studies

A mixture of the coal tar pitch and 3wt% of $SnCl_2 \bullet 2H_2O$ was heated in a capsule to 850°C to simulate the effects of electrode baking. After heat treatment we measured an 83% yield compared to a yield of 73% for the pitch heated similarly without the additive. An elemental analysis of the baked pitch/$SnCl_2 \bullet 2H_2O$ product showed that all the Sn but very little of the Cl had been retained after the 850°C baking.

5. Properties of Electrodes Produced With the Pitch/$SnCl_2 \bullet 2H_2O$ Binder

Results are summarized in Tables III and IV. The 150mm-diameter electrodes demonstrate that $SnCl_2 \bullet 2H_2O$ has a positive effect on the coking yield of the coal tar binder pitch and the bake bulk density (BD) at the 95% confidence level. In addition, $SnCl_2 \bullet 2H_2O$ has no adverse effect on the green BD. The increased BD, however, becomes less profound after graphitization, attributable to the loss of tin. Table IV presents graphite property data including BD, electrical resistivity (SR), flexural strength (FS) and coefficient of thermal expansion (CTE). The graphite density increase by $SnCl_2 \bullet 2H_2O$ is significant at the 95% confidence level. The effect of $SnCl_2 \bullet 2H_2O$ on strength, however, is negative.

Table III. Green Through Bake Stage Property Summary

	Green BD (g/cm^3)	Bake BD (g/cm^3)	Coking Yield (%)
Control	1.748	1.641	67.3
3wt% $SnCl_2 \bullet 2H_2O$/Pitch	1.748	1.671	72.5
Difference	--	**0.030**	**5.2**

Note: Bold number denotes significant at the 95% confidence level.

Table IV. Graphite Property Summary

	Graphite Properties						
	BD (g/cm^3)	wg SR (μΩm)	ag SR (μΩm)	wg FS (psi)	ag FS (psi)	wg CTE (1/°C)	ag CTE (1/°C)
Control	1.682	5.731	8.906	1547	994	0.264	1.402
3wt% $SnCl_2 \bullet 2H_2O$/Pitch	1.699	5.597	9.012	1425	893	0.228	1.300
Difference	**0.017**	-0.134	0.106	-122	-101	-0.036	-0.102

Note: wg = parallel to extrusion direction; ag = perpendicular to extrusion direction. Bold number denotes significant at the 95% confidence level.

Discussions

It is apparent that $SnCl_2 \bullet 2H_2O$ is an extremely effective coking catalyst for pitch. As little as 1.5% addition can increase the pitch carbon yield by nearly 8% (after accounting for retained Sn). The reaction process however appears to be complex.

Thermal analysis measurements show that the $SnCl_2 \bullet 2H_2O$ is molten at the 160°C mix temperature and begins to lose two moles of water as the temperature increases. At about 250°C all the water of hydration is eliminated allowing reaction of anhydrous $SnCl_2$ with low molecular weight pitch components such as anthracene.

Because of the small amount required it appears that $SnCl_2$ is acting as a true coking catalyst. Our inability to detect any HCl during reaction using mass spectrometry indicates the occurrence of an oxidative process in which the Sn^{++} is reduced to metallic Sn with the evolution of Cl_2. Aromatic hydrogen transfer and ring cleavage reactions also seem to be involved.

Despite the large increases in pitch carbon yield, we were unable to detect any improvement in graphite strength. This result could be attributable to the evolution of additive components during baking and graphitization. However, the unique effects demonstrated for the $SnCl_2 \bullet 2H_2O$ demonstrate the potential for the use of chemical additives for altering the carbonization process.

Conclusions

1. $SnCl_2$ was found particularly effective in increasing pitch coking yield without excessively affecting viscosity at the mixing temperature.
2. $SnCl_2$ reacts with aromatic hydrocarbons to affect polymerization.
3. The expected increases in binder carbon yield and final graphite density were demonstrated at the 95% confidence level.
4. No improvement in graphite strength was achieved most probably due to structural disruption by H_2O and chlorine gas evolution during pitch carbonization and loss of tin during graphitization.

References

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