

RHEOLOGICAL CHARACTERISATION OF STANDARD AND CUT-BACK ANODE PITCHES

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INTRODUCTION

Binders for anodes used in aluminium electrolysis are coal tar pitches. Søderberg anodes are self-baking and only gravity and a small hydrostatic pressure of molten paste are the forces "compacting" the anode prior to baking. The viscosity development in the binder phase with temperature plays an important role during this process. To meet the demand for Søderberg pitches, particularly with so-called dry anode technology, several pitch producers have developed vacuum distilled pitches. They are normally vacuum distilled to a softening point (t_{sp}) in the range 115-130°C Mettler, contain no or insignificant amounts of optical mesophase, have the required thermal stability, and high coke yields. A significant amount of light polyaromatic hydrocarbons (PAH) is nevertheless still retained in the pitches, which can be emitted to the environment. Environmental legislation and regulations have focused on such PAH emissions thus making it necessary to find alternative binders or to modify the existing ones with respect to PAH content. Petroleum pitches might be an alternative, but their more aliphatic nature tend to give a poorer binder coke and a lower quality anode. Another possibility is to vacuum distil coal tar pitches to very high softening points, thus stripping off a significant part of the PAH content. They may then be refluxed with non-PAH oils or distillate fractions back to softening points compatible with existing mixers. These are the so-called cut-back pitches. The paper discusses viscosity characterisation of cut-back and petroleum pitches as well as standard vacuum distilled anode binders in the temperature range from about 20-120°C above t_{sp} .

EXPERIMENTAL

Pitch viscosities were measured on a Haake Rotovisco RV20 with an M5 measuring system and cylindrical (not coaxial) sensors, modified to increase the upper operational temperature to 250°C. The viscometer was calibrated with oil standards of known viscosity. An amount of 220g pitch was added to the sample holder and melted on a temperature controlled oil bath. The measurements started at the highest temperature, which was stepwise reduced and equilibrated before each new measurement. The temperature stability was better than $\pm 0.1^\circ\text{C}$ during each measurement series. At each temperature a set of viscosity measurements were performed by stepwise variation of the shear rate. Starting with a high sensor rpm the shear rate was first reduced, then increased again. Within the shear rate and temperature ranges applied all pitches displayed Newtonian behaviour. A total of 18 pitches from three different producers (A,B,C)

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were investigated. They included 9 standard vacuum anode pitches, 6 cut-back pitches and 3 petroleum pitches with t_{sp} ranging from 109.2-142.5°C Mettler (Table 1).

RESULTS AND DISCUSSION

One aim of the work was to arrive at an isoviscous mixing temperature (t_{mix}). Paste plant mixing equipment tends to put a practical upper limit to the softening temperature of anode binders. This t_{mix} was determined by fitting the viscosity data ($\log\eta$) and temperature ($1/T$) to a 2nd order polynomial (Figure 1). The pitch viscosity was chosen as the viscosity at 210°C (a practical upper temperature limit of the mixer) of the pitch with highest t_{sp} (A6). This corresponds to a binder viscosity of 0.804 Pas, and t_{mix} for all other pitches were calculated at this constant viscosity (Table 1). The temperature difference between t_{sp} and t_{mix} was found to be highest for cut-back pitch B2 (79.3°C) and lowest for vacuum pitch A1 (63.5°C) which has to be considered if anode paste is mixed under similar rheological conditions. It is also seen from Table 1 that cut-back pitches and petroleum pitches must be heated to a higher temperature relative their t_{sp} to reach this isoviscous t_{mix} .

An Arrhenius' type plot of $\log\eta$ versus $1/T$ (Figure 1) serves mainly to separate the pitch viscosity curves with respect to

Table 1. Pitch data and constants calc. from the WLF eqn.

Pitch type	t_{sp} Mettler (°C)	t_{mix} (°C)	WLF equation			C2/C1	
			C1	C2	t_g (°C)		
Anode	A1	119.2	182.7	16.10	34.90	77.3	2.17
vacuum	A2	133.1	200.5	16.17	39.07	85.2	2.42
pitches	A5	131.8	198.8	16.31	40.01	84.5	2.45
	A6	142.5	210.0	15.86	35.59	96.4	2.24
	A7	119.7	184.6	15.93	33.60	79.8	2.11
	B1	123.0	190.1	16.33	40.18	75.7	2.46
	B4	118.4	186.3	16.03	36.55	74.2	2.28
	C1	122.4	190.7	16.08	37.40	77.5	2.33
	C2	116.6	182.8	15.88	33.70	75.1	2.12
Cut-back	A3	122.4	192.3	16.61	46.60	67.7	2.81
	A4	132.0	204.0	16.62	46.84	79.2	2.82
	B2	130.7	210.0	18.23	74.62	63.4	4.09
	B3	131.6	202.7	16.83	50.02	75.2	2.97
	B5	116.1	188.5	16.90	50.19	62.3	2.97
	B6	122.4	193.2	16.85	49.79	66.8	2.96
Petroleum	A8	120.3	190.9	17.45	59.00	57.8	3.38
	A9	112.3	181.8	17.05	51.97	55.0	3.05
	B7	109.2	186.6	17.69	67.44	40.6	3.81

t_{sp} within this temperature range. More subtle, but no less important, differences such as the slope of the curves (rate of change in activation energy of viscous flow), can hardly be seen in these plots.

A widely used viscosity-temperature relationship that can be interpreted in terms of free volume concepts is the Williams-Landel-Ferry equation (WLF)¹:

$$\log \eta = \log \eta_g - \frac{C_1(T - T_g)}{C_2 + T - T_g} \quad (1)$$

In our case the glass transition temperature T_g (Kelvin) was chosen as the reference temperature. C_1 and C_2 are constants and η_g is the viscosity at T_g . By assuming $\eta_g = 10^{12}$ Pas, Eqn.(1) can be written:

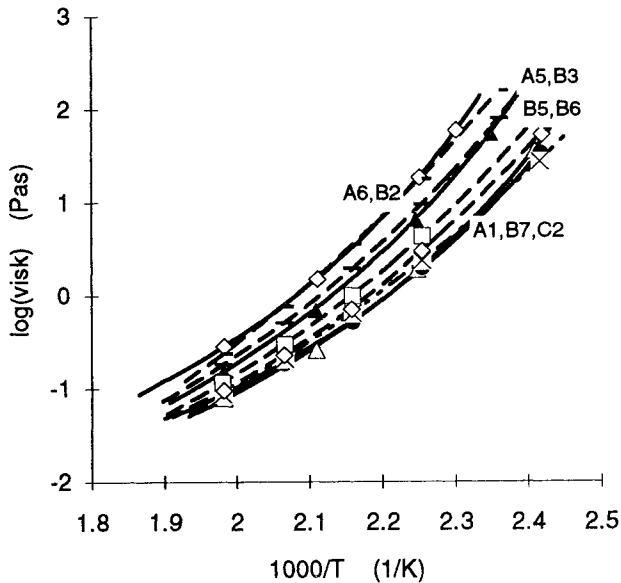


Figure 1. Arrhenius' type plots of some of the η - T data.

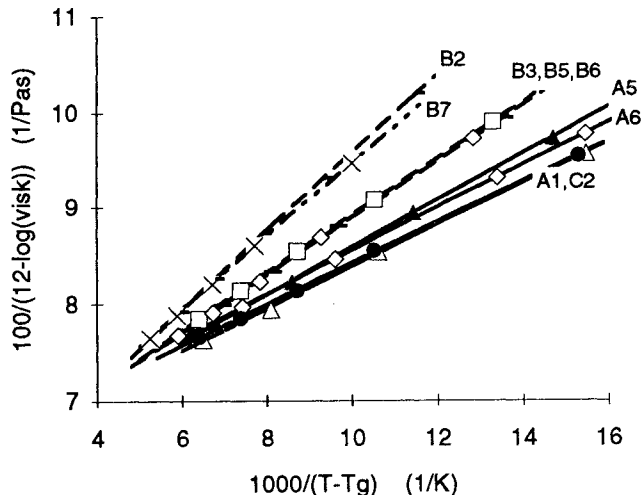


Figure 2. The same data sets shown in the previous figure fitted to the WLF equation and plotted on its linear form.

$$12 - \log \eta = \frac{C_1(T - T_g)}{C_2 + T - T_g} \quad (2)$$

and the constants C_1 , C_2 and T_g found by curve fitting to experimental data. Results are shown in Table 1 for all 18 pitches. The same pitch viscosity data plotted on the linear form of WLF:

$$\frac{1}{12 - \log \eta} = \frac{1}{C_1} + \frac{C_2}{C_1(T - T_g)} \quad (3)$$

are shown in Figure 2. The slopes are given by the C_2/C_1 ratios and have a characteristic range for each pitch type (Table 1): 2.1-2.5 for vacuum distilled pitches, 2.8-3.0 for cut-back pitches (with one exception of 4.1), and 3.1-3.8 for petroleum pitches. This ratio seem to reflect the molecular weight composition of the pitches, i.e. most "pitch-like" for the vacuum anode pitches and most "tar-like" for the petroleum pitches¹. The cut-back pitches have been refluxed with low molecular weight oils and populate an intermediate C_2/C_1 range. Pitch B2 is, according to PAH analysis², the cut-back pitch that has been subjected to the most severe distillation. Its high C_2/C_1 ratio may reflect the relatively larger amount of reflux oil that have been used to bring its t_{sp} back to normal. Work is in progress to see whether the C_2/C_1 ratio can reliably be used to characterise the distillation conditions during production of cut-back pitches, and whether the t_{sp} prior to reflux can be quantified.

CONCLUSIONS

The temperature sensitivity of binder viscosities should be determined to get reproducible anode mixing conditions, especially when standard vacuum anode pitches are replaced with low-PAH cut-back binders.

The C_2/C_1 ratio derived from fitting η - T data to the WLF equation seem to be a useful parameter for characterising anode binders in the mixing temperature range.

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