USE OF PETROLEUM RESIDUES AS BINDER PITCHES - - RELATION OF FIXED CARBON AND SOFTENING POINT OF PITCH WITH COMPONENT PROPERTIES AND CORRELATION OF BINDING POWER WITH FIXED CARBON OF ITS COMPONENTS

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1. INTRODUCTION

The purpose of this experimental program was three-fold:-

(a) to determine the relationship between the fixed carbon (FC) content of a pitch with the FC of its component parts.
(b) to determine the relationship between the softening point (SP) of a pitch and the SP of its component parts.
(c) to determine if a relationship exists between the binding strength of a pitch, when used as an electrode binder, and the FC properties of its component parts.

2. EXPERIMENTAL

Four petroleum products were selected to be used to make pitches which were used as the basis for the test program. These basic products were vacuum residue from Gach Saran Crude (G), vacuum residue from Arabian Light Crude (L), Decant Oil from a fluid catalytic cracker (F), ethylene plant tar from a naphtha cracking plant (N). And a commercial binder pitch made from coal tar (T) was also included for comparison.

Each of these feeds were heat-treated at 420-440°C from 10 to 240 minutes to make pitches which were solvent fractionated into the following three fractions shown as Figure 1:

(i) Benzene insolubles (A fraction)
(ii) Benzene soluble but n-heptane insolubles (B fraction)
(iii) n-heptane solubles (C fraction)

The fixed carbon (FC) and softening point (SP) of each whole pitch and each fraction were tested. These test results are shown in Table 1 along with the weight percent of each fraction. FC was measured by Japan Industrial Standard JIS K 2425 which is similar to ASTM method No. D 2416. In this test the quantity of residual or fixed carbon is determined after the sample has been heated at 800°C for 30 minutes. SP was measured using a micro melting point procedure as developed by National Industrial Research Institute of Kyushu.

Afterwards each pitch was blended with electrode grade coke and heated to 1,000°C to make a electrode test piece for strength testing. The compressive strength of each test piece made with the various pitches is also included on Table 1.

3 RESULTS AND DISCUSSION

An attempt was made to determine what was the relationship between the FC of the whole pitch and the weighted average FC of its three fractions. Figure 2 shows plot of the sum of the weighted averages of the fraction FC vs. the FC of the whole pitch. It can be seen that it is necessary to add a correction factor, α, to the weighted average sum of the products FC to make it equivalent to the FC of the whole pitch. As seen from Figure 2, the value of α calculated is approximately 7.2 such that the following relationship can be written:

$$FC_{Pitch} = (FC_A)(A) + (FC_B)(B) + (FC_C)(C) + \alpha \quad \ldots\ldots (1)$$

where,
(1) FC_{Pitch}, FC_A, FC_B and FC_C are the test values of fixed carbon of the pitch and its three fractions, and,
(2) α is the correction factor. (approx. 7.2)

The need for α is probably due to the effect of mutual interaction between each fraction during carbonization of pitches.

As a second experiment, an attempt was made to develop a relationship between the SP of the whole pitch and its three fractions. However, the SP of the A fraction was too high to measure, being above 400°C. Therefore, the following regression equation was used for a trial test with a pseudo SP (SP ps.) for the A fraction:

$$SP_{Pitch} = (SP\ ps.)(A) + (SP_B)(B) + (SP_C)(C) + \beta \quad \ldots\ldots (2)$$

where SP_B and SP_C are the values of the SP of the B & C fractions, respectively, and β is a constant.

Regression results based on the above formula show $SP_{ps.}$ to be 413 and β to be -96. A plot of **observed** SP_{Pitch} values vs. calculated values using the above formula is shown in Figure 3. This relationship shows a good correlation factor of 0.94. As with α in the FC relationship, the need for β as a correction factor is considered to be the effect of chemical and/or physical interaction between each fraction.

As a final goal an attempt was made to develope a relationship which would predict pitch binding capability, when used as an electrode binder, with component FC property. Basis a regression analysis it was found that the following three factors have a strong statistical relationship with the binding strength of pitch:

(i) The average FC of fractions A and B
(ii) The difference between FC_A and FC_B
(iii) B, the wt. fraction of benzene solubles/n-heptane insolubles

As such, the following equation was found to give the best estimate of pitch binding strength, which is defined as, F-value:

$$F = \left[\frac{FC_A + FC_B}{2} + (FC_A - FC_B)\right] \times (B) \quad \ldots\ldots\ldots (3)$$

Values of F calculated from the above formula for the pitches tested have been listed in Table 1 next to the compressive strength of the electrode using this pitch as a binder. The relationship between F-value and electrode strength has been plotted in Figure 4. This correlation seems to be reasonably predictive, having a correlation factor of 0.87.

Table 1 Properties of pitches and its fractions

Symbol	Heat treatment condition (°C)	Heat treatment condition (min.)	Pitch C/H Ratio Atom.	Pitch FC (wt%)	Pitch SP (°C)	Fractions Yield (wt.%) A	Yield B	Yield C	FC (wt.%) A	FC B	FC C	SP (°C) B	SP C	Bind'g power Comp.1) Strength	Bind'g power F- 2) value (x 10)
G	430	60	1.09	58.8	132	33.6	21.8	44.6	71.5	71.4	28.1	225	30	530	156
La	420	120	1.15	59.6	107	34.0	20.3	45.7	71.6	71.8	27.8	300	30	370	145
Lb	430	60	1.16	59.4	129	32.5	27.1	40.4	69.0	73.0	29.8	300	42	690	182
Lc	440	34	1.26	63.8	141	36.9	23.7	39.4	69.3	75.4	33.9	300	52	500	157
Ld	430	80	1.40	71.1	208	53.5	17.8	28.7	75.5	64.1	35.7	300	48	75	144
Na	420	15	1.29	59.9	132	24.4	35.1	40.5	78.2	68.7	27.8	300	37	860	291
Nb	430	10	1.34	59.7	129	20.6	39.8	39.6	72.5	70.5	28.1	300	60	960	293
Nc	430	60	1.50	69.1	164	47.4	23.0	29.6	72.1	68.1	27.9	300	50	410	170
Fa	430	150	1.45	49.4	57	25.6	28.7	45.7	66.3	59.1	17.3	125	30	380	201
Fb	430	210	1.53	53.6	74	30.2	28.8	41.0	72.0	60.3	17.1	115	30	720	224
Fc	440	120	1.57	55.3	82	32.8	29.4	37.8	74.6	57.0	17.5	110	30	950	245
T	-	-	1.79	60.9	99	30.5	43.6	25.9	78.3	57.4	16.6	120	30	910	387

1) Compressive strength of baked carbon block (kg/cm^2), 2) Calculated by equation (3)

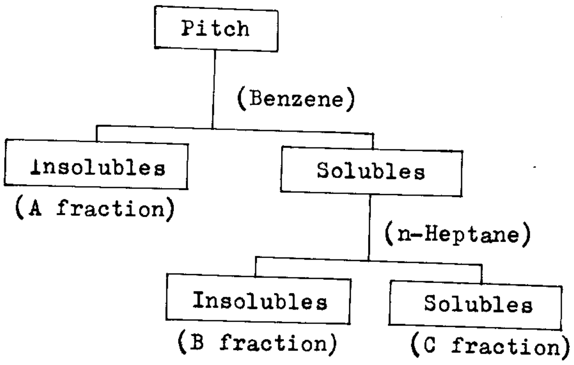

Fig. 1 Fractionation scheme

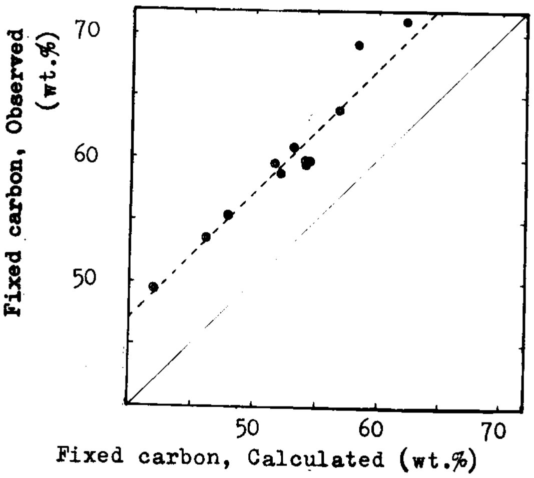

Fig. 2 Relation of FC, Actual and Calculated

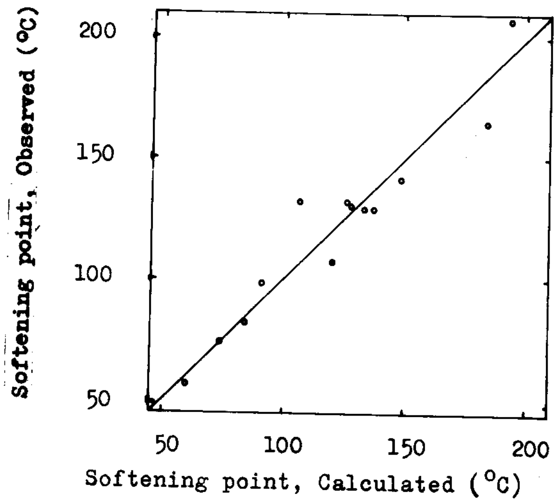

Fig. 3 Relation of SP, Actual and Calculated

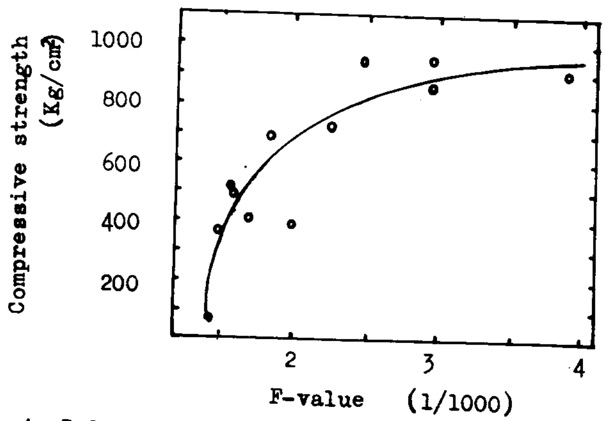

Fig. 4 Relation of F-value vs. compressive strength