

SOLVENT FRACTIONATION OF ELECTRODE BINDER PITCHES

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INTRODUCTION

Solvent fractionation has been used fairly extensively for studying composition and structure of pitches. Among the more recent papers published on the subject are those of Wood and Phillips, (1) Mallison, (2) Franck, (3) and Lissner and Schäfer. (4) However, most of the studies dealt with a small number of samples and rather elaborate fractionation techniques. Past experience in our own laboratory has indicated that there is danger in studying too few samples: the conclusions drawn can be greatly influenced by the types of pitch used or by the treatment the pitch has undergone. For these considerations, and also because the time involved even for simple fractionation is always fairly long, it was preferred to try a fractionation procedure which would be relatively simple in operation as well as in number of fractions produced, thus allowing the coverage of a large number of binders. A two-stage fractionation, which would permit isolation of the much-discussed carbon-I (C-I), appeared appropriate.

EXPERIMENTAL

Choice of Solvents

In order to select the most suitable fractionation agents, 14 solvents were examined. The procedure employed consisted in refluxing 1 gram of pitch in 100 ml of solvent for one hour, and determining the amount of the undissolved material collected on a fritted porcelain filtering crucible. In tests with high boiling point solvents such as quinoline and nitrobenzene, the sample was digested only (no refluxing) in the solvent at 80-90° C on a steam bath. The results of solubility tests on five coal-tar pitches ranging in melting point from 92 to 180° C are shown in Table 1.

TABLE 1
SOLUBILITY OF PITCH IN SOLVENTS

Solvents	Percent Solubility					Average
	92° C Pitch	100° C Pitch	108° C Pitch	127° C Pitch	180° C Pitch	
Quinoline	71	93	90	82	71	81
Nitrobenzene	66	88	84	67	57	72
Pyridine	61	88	82	67	59	71
Chloroform	52	68	68	55	46	58
Toluene	53	70	68	53	44	58
Benzene	50	67	66	56	40	56
Carbon Tetrachloride	45	58	54	38	27	44
Acetone	44	56	50	31	28	42
Buryl Alcohol	33	40	39	27	19	32
n-Heptane	25	25	22	15	7	19
Isopropyl Alcohol	20	27	22	11	7	17
n-Hexane	19	17	15	9	6	13
Methyl Alcohol	16	19	15	7	4	12
Petroleum Ether	10	8	8	9	4	8

Of the solvents examined, quinoline and acetone were selected for various reasons. Quinoline appeared to be the solvent having the strongest dissolving power and, as such, would isolate the least soluble fraction usually referred to as carbon-1. Acetone was chosen because it appeared to provide a fair distribution of the pitch quinoline-soluble portion into two fractions; furthermore, acetone, because of its high volatility, can be driven off easily at low temperature.

Fractionation Procedure

A sample size of 20 grams was found adequate in most cases to provide fractions in sufficient quantity to permit their analysis.

Hard binders were ground to pass a 65 mesh sieve. Soft binders were slightly heated for easier manipulation.

Acetone-Soluble Fraction

Since it was inconvenient to carry out the extraction in one operation on account of the considerable quantity of acetone, equivalent to the proportion employed in the solubility tests, successive extractions were carried out to complete the separation of the acetone-soluble fraction. With 20 grams of starting binder material, three extractions, with 500 ml of acetone each, were generally sufficient. Between extractions, the acetone solution was filtered off, the residue washed with acetone and dried. During the first, and occasionally also during the second extraction, part of the pitch softened and formed agglomerates; consequently it was necessary to grind the residue between extractions. Soxhlet extraction was attempted on a few pitches, but the agglomeration was even worse. The filtration was carried out on a specially made aluminium filter support with a detachable top light enough to be weighed on an analytical balance. A combination of a double layer of glass-fiber filter paper and one analytical filter paper disk was used as filtering medium.

To recover the acetone-soluble portion from the filtrates and washings, the bulk of the acetone was removed by careful distillation. Occasionally, the solution showed tendency to bump, even when "Boileezer" stones were added; it was therefore preferable to remove the acetone simply by slow evaporation. In either case, the concentrated solution was finally transferred to a tared vessel and the remaining acetone removed by evaporation in a vacuum oven.

Quinoline-Insoluble Fraction

The residue from the acetone extraction was ground to a fine powder in a glass mortar and digested with quinoline on a steam bath while stirring. In the preliminary work, a constant amount of quinoline was used for all pitches. However, it was observed that the filtration rate varied, depending on the pitch type, from fast to zero; the filtration was especially difficult with heat-treated or cut-back pitches. This difficulty was overcome, and fast filtration obtained, by using a quantity of quinoline proportional to the expected percentage of the intermediate fraction (quinoline-soluble, acetone-insoluble); this percentage was calculated by deducting from the known acetone-insoluble content, the amount of quinoline-insoluble determined by an analytical standard procedure on a small sample.

For filtration, the same type of filtering set-up as specified for the acetone-soluble fraction was used. The quinoline-insoluble residue was washed with quinoline and acetone, dried and weighed.

Quinoline-Soluble, Acetone-Insoluble Fraction

The recovery of this intermediate fraction from the filtered quinoline solution presented some difficulty. It was found impossible to get rid completely of the quinoline by distillation at atmospheric pressure or even under vacuum without excessive heating of the residue. A procedure was finally worked out whereby the bulk of the quinoline was first removed by gentle distillation at atmospheric pressure, followed by evaporation in an open dish on a steam bath until a suitable concentration was attained. The concentrated solution was then poured slowly while stirring into acetone; the extent to which the quinoline solution was concentrated prior to precipitation, and the volume of acetone used were proportional to the amount of solute. A dense, almost crystalline precipitate formed which was easily filtered. After filtration, it was ground to a fine powder, re-extracted with acetone, re-filtered and dried. After this treatment, there was no trace of quinoline odour and it was assumed that the solvent was completely removed. Because of practical difficulties, no attempt was made to recover the very small amount of solute which remained in the filtrate.

A flow diagram illustrating the complete fractionation technique is given in Figure 1.

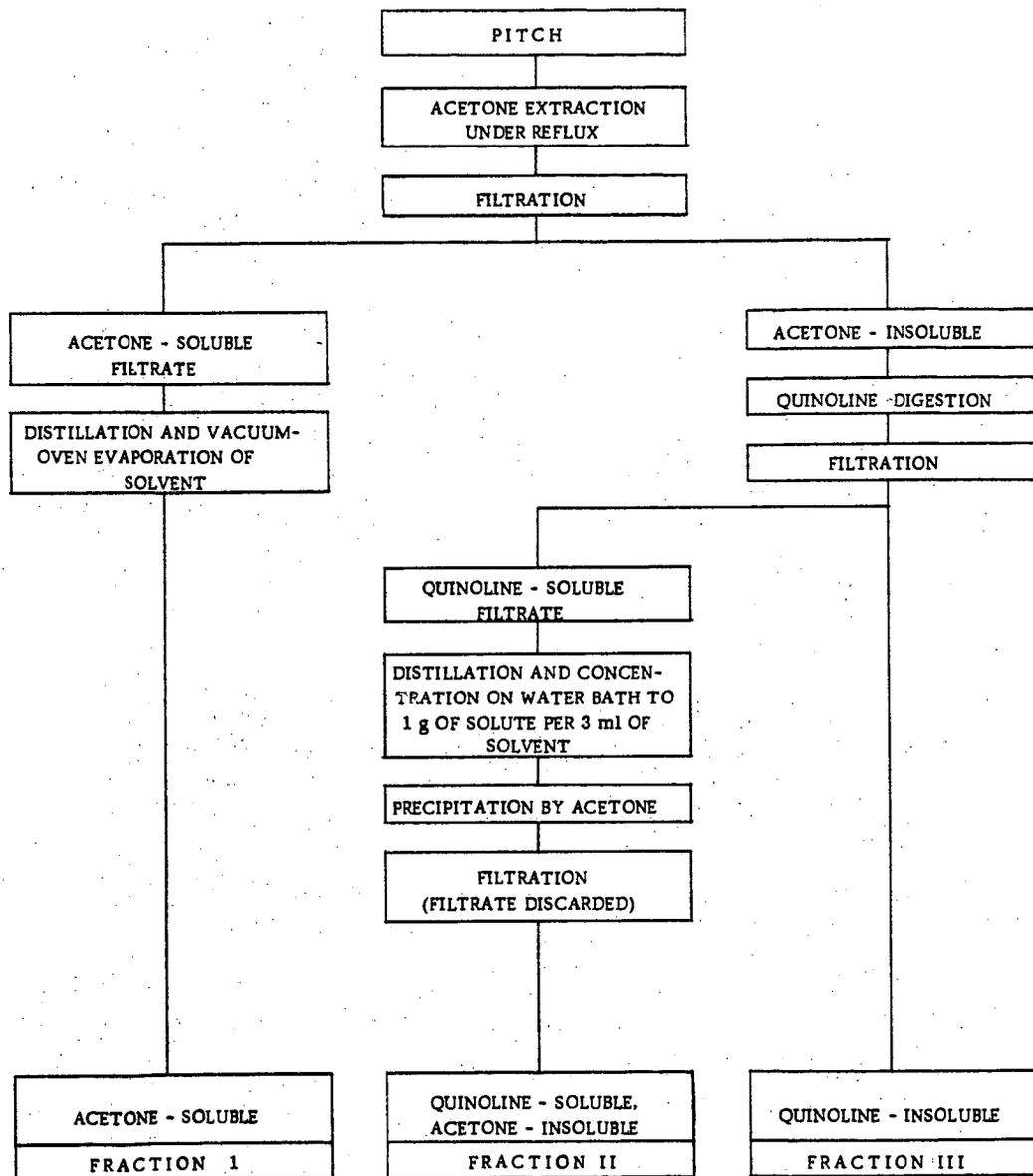


FIGURE 1

FRACTIONATION SCHEME

RESULTS

The samples of binder pitch selected for this investigation represented different types of pitch, different producers and different levels of quality. They are listed in Table 2 which also contains some of their properties.

In all, 26 samples were fractionated: 14 straight-distilled pitches; three heat-treated pitches; six cut-back pitches, i. e. pitches which had been produced by blending heat-treated pitches with some light materials such as oil or tar; one chemically-treated pitch prepared from straight-distilled pitch by digesting with 2% sulphur; and finally two petroleum pitches. Twelve additional regular production petroleum pitches, all from the same source, were also fractionated, but only one is reported since identical observations were made on all. Consequently, it should be borne in mind that conclusions drawn and observations made on regular production petroleum pitches are based effectively on a fairly large number of samples and not only on sample J-1.

Fractionation results and some characteristics of pitch fractions are presented in Table 3.

DISCUSSION

Acetone-Soluble Fraction

The acetone-soluble fraction is a dark brown, almost black material which at room temperature has a consistency ranging from that of tar or very heavy grease to that of solid pitch. Thus, there is a noticeable difference in viscosity for fractions obtained from different pitches, as shown by the equiviscous temperatures given in Table 3. The coking value of the fraction is low, but also covers a fairly wide range; in general, it is lower for cut-back binders than for straight-distilled pitches of equivalent softening point. It is also of some interest to note that the coking value of the acetone-soluble fraction for regular production petroleum pitches, exemplified by sample J-1, is higher than for any of the coal-tar pitches, although the carbon-hydrogen ratio is significantly lower.

Only the acetone-soluble fraction was found suitable for viscosity determination. As shown in Figure 2, there is a definite trend for the temperature coefficient of whole pitches to decrease with larger differences between the equiviscous temperature at 15 poises of the whole pitch and that of the acetone-soluble. The only real exception is the experimental petroleum sample J-2; difficulty experienced with this pitch in preparing mix for test electrodes might be explained at least in part by this deviation, which is the result of the very low equiviscous temperature of the acetone-soluble as compared to the high equiviscous temperature of the whole pitch. On the basis of present knowledge, it can be hypothesized that this petroleum pitch was produced by severe cracking of a petroleum crude and dilution of the residuum with light material to obtain the desired melting point.

The relationship between coking value of the acetone-soluble fraction and its equiviscous temperature, shown in Figure 3, illustrates some interesting facts. The acetone-soluble fractions of four of the six cut-back pitches are characterized by low coking value - approximately 15% - and low equiviscous temperature - approximately 52° C. Considering the melting point level of these pitches, it can be reasonably assumed from this relationship that they were produced by diluting high softening point binders presumably with very light materials such as "oils"; this is a process by which binders of low quality can be expected to result. Straight-distilled pitch C-2 also contains an acetone-soluble fraction exhibiting low coking value and low equiviscous temperature, and yet is not a cut-back pitch; in this instance, it should be remembered that the softening point of C-2 is very low compared to those of cut-back pitches mentioned above and consequently, there is no discontinuity between the acetone-soluble characteristics and those of the whole pitch. Samples A-4 and C-7 are also cut-back pitches, but the material used for diluting was tar, which explains the higher figure for coking value and equiviscous temperature of their acetone-soluble.

Quinoline-Soluble, Acetone-Insoluble Fraction

The quinoline-soluble, acetone-insoluble fraction consists of a black-brown brittle substance which can be pulverized easily. Upon heating, it does not melt although it shows some tendency to fuse. Its carbon-hydrogen ratio is somewhat higher than that of the whole binder, and does not show much variation; there is, however, a noticeable difference between the fractions from binders of coal-tar and petroleum origin, the latter having a lower carbon-hydrogen ratio. The same applies to the coking value; it is lower for petroleum pitches, with the exception of the experimental one, than for binders of coal-tar origin.

TABLE 2

DESCRIPTION OF PITCH SAMPLES

Sample Identification ^(a)	Compressive Strength of Test Electrodes kg/cm ²	Melting Point °C	Coking Value %	C-I (Quinoline-Insoluble) %	Atomic Carbon-Hydrogen Ratio	Density g/cc	Viscosity Data ^(b)		
							EVT ₁₅	EVT ₁₀₁₅	Temperature Coefficient poises/°C
<u>COAL-TAR STRAIGHT-DISTILLED PITCHES</u>									
A-1	430	111	61.6	14.0	1.97	1.35	162	123	25.6
B-1	382	109	59.8	15.7	1.91	1.36	165	124	24.4
C-1	365	95	57.7	16.7	1.93	1.35	149	108	24.4
D-1	361	108	59.4	23.1	1.84	1.36	170	126	22.7
E-1	360	107	59.4	13.7	1.85	1.34	158	118	25.0
F-1	354	108	58.2	9.9	1.72	1.33	166	127	25.6
C-2	354	50	44.5	13.4	1.76	1.28	86	54	31.2
C-3	351	112	56.2	6.5	1.80	1.32	172	131	24.4
A-2	347	95	55.5	3.4	1.74	1.32	149	114	28.6
G-1	320	100	53.1	7.4	1.68	1.30	150	110	25.0
G-2	320	88	53.5	10.0	1.82	1.32	141	102	25.6
H-1	296	69	44.1	6.8	1.66	1.24	111	78	30.3
C-4	274	93	51.4	5.8	1.73	1.33	147	110	27.0
I-1	257	93	49.7	4.9	1.62	1.31	147	111	27.8
<u>COAL-TAR HEAT-TREATED PITCHES</u>									
C-5	444	138	65.6	14.2	1.86	1.33	207	158	20.4
A-3	410	129	67.3	21.3	1.92	1.35	204	152	19.2
C-6	339	102	56.8	11.5	1.78	1.32	162	119	23.2
<u>COAL-TAR CUT-BACK PITCHES</u>									
A-4	376	102	56.0	14.2	1.67	1.32	162	121	24.4
C-7	354	105	57.2	9.8	1.79	1.32	166	125	24.4
I-2	313	104	55.7	14.2	1.68	1.32	170	123	21.3
I-3	309	104	53.9	18.9	1.69	1.33	158	115	23.2
I-4	275	102	56.5	17.9	1.70	1.32	166	115	19.6
A-5	165	107	60.9	28.9	1.80	1.34	175	117	17.2
<u>COAL-TAR CHEMICALLY-TREATED PITCH</u>									
A-6	246	100	49.6	4.7	1.59	1.30	153	115	26.3
<u>PETROLEUM PITCHES</u>									
J-1 regular production	300	109	55.6	19.0	1.46	1.28	166	127	25.6
J-2 experimental	-	132	56.7	14.6	1.49	1.30	209	155	18.5

(a) Letters indicate different suppliers.

(b) EVT refers to equiviscous temperature i. e. the temperature at which a pitch has a specified viscosity. EVT₁₅ and EVT₁₀₁₅ correspond to viscosities of 15 and 1015 poises respectively.

Temperature coefficient of viscosity is obtained from the following expression: $1000/(EVT_{15} - EVT_{1015})$.

Note: Analytical data were obtained by Aluminium Laboratories Limited internal methods.

TABLE 3

FRACTIONATION RESULTS AND CHARACTERISTICS OF FRACTIONS.

Sample Identification	% Fraction			% Coking Value			Atomic C/H			Density, g/cc			EVT ₁₅ , °C
	I	II	III	I	II	III	I	II	III	I	II	III	
<u>COAL-TAR STRAIGHT-DISTILLED PITCHES</u>													
A-1	44.1	42.8	13.1	26.8	88.4	98.8	1.60	2.03	4.26	1.24	1.37	1.62	72
B-1	46.0	39.1	14.9	20.5	90.4	98.9	1.54	2.04	4.55	1.20	1.43	1.63	66
C-1	47.1	37.3	15.6	20.4	88.8	97.9	1.58	2.01	4.03	1.23	1.37	1.60	63
D-1	48.4	29.5	22.1	22.8	89.2	97.9	1.41	1.91	4.26	-	1.34	1.62	79
E-1	47.4	39.2	13.4	22.2	89.4	99.1	1.56	1.96	4.48	1.23	1.39	1.63	74
F-1	51.9	38.4	9.7	24.8	87.5	97.0	1.49	1.94	4.52	1.23	1.39	1.65	79
C-2	61.0	25.7	13.3	16.4	87.3	97.6	1.50	2.01	4.27	1.21	1.38	1.63	40
C-3	49.9	44.1	6.0	22.2	91.2	96.6	1.50	2.06	4.18	1.22	1.39	1.63	66
A-2	56.2	40.5	3.3	21.7	91.0	97.7	1.54	2.04	4.20	1.22	-	-	72
G-1	57.4	35.6	7.0	23.5	91.1	97.0	1.45	1.95	3.77	1.23	1.37	1.59	80
G-2	54.2	36.8	9.0	19.7	90.7	98.6	1.50	2.00	4.05	1.23	-	-	62
H-1	67.2	26.8	6.0	19.0	88.8	99.1	1.44	1.90	3.73	1.21	-	-	58
C-4	57.7	37.1	5.2	20.3	90.5	97.3	1.51	2.03	3.77	1.23	1.40	1.61	69
I-1	60.9	34.0	5.1	20.0	90.9	97.1	1.42	1.98	3.40	1.21	1.38	1.55	63
<u>COAL-TAR HEAT-TREATED PITCHES</u>													
C-5	42.9	44.8	12.3	26.6	91.7	96.0	1.56	2.05	2.96	1.26	1.33	1.51	93
A-3	37.1	43.5	19.4	19.1	92.8	96.4	1.58	2.15	3.19	1.23	1.39	1.52	77
C-6	51.5	38.2	10.3	20.3	93.2	98.7	1.50	2.07	2.95	1.21	1.39	1.50	67
<u>COAL-TAR CUT-BACK PITCHES</u>													
A-4	52.8	34.6	12.6	21.9	91.3	96.9	1.43	1.97	2.52	1.21	1.37	1.44	63
C-7	51.6	40.0	8.4	19.3	92.0	96.4	1.54	2.13	3.30	1.22	1.29	1.55	68
I-2	49.9	36.5	13.6	14.9	93.1	97.4	1.40	1.95	2.62	1.20	1.26	1.46	51
I-3	52.6	29.9	17.5	16.1	93.4	98.0	1.45	1.93	2.48	1.19	1.26	1.44	53
I-4	50.3	33.5	16.2	16.3	92.0	98.3	1.42	2.00	2.55	1.20	1.22	1.28	54
A-5	44.5	27.7	27.8	14.4	94.3	97.9	1.49	2.12	2.54	1.22	1.37	1.45	53
<u>COAL-TAR CHEMICALLY-TREATED PITCH</u>													
A-6	59.4	36.8	3.8	19.9	88.0	94.5	1.47	1.88	3.25	1.20	-	-	69
<u>PETROLEUM PITCHES</u>													
J-1	53.9	25.7	18.4	27.4	83.4	96.1	1.20	1.58	3.01	-	1.35	1.51	72
J-2	47.3	39.0	13.7	18.1	92.0	97.0	1.16	1.78	2.46	1.14	1.31	1.51	45

I = Acetone-Soluble.

II = Quinoline-Soluble, Acetone-Insoluble.

III = Quinoline-Insoluble.

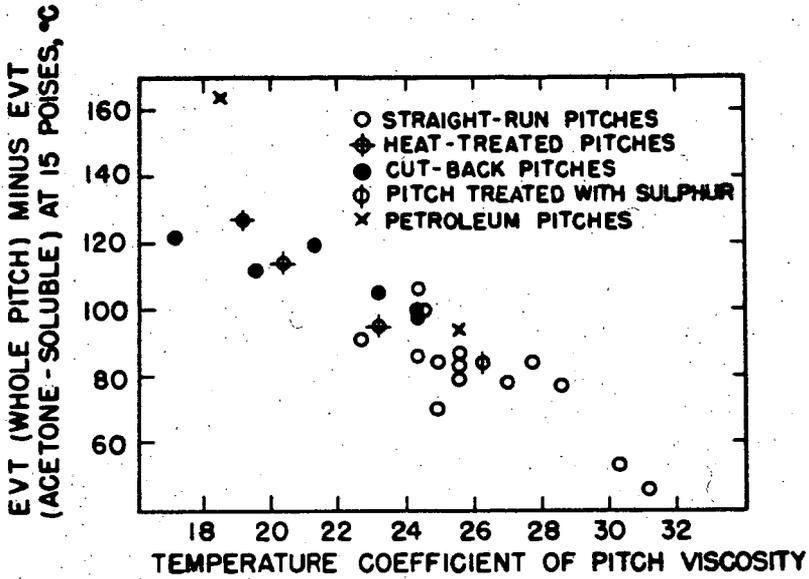


FIGURE 2

RELATIONSHIP OF VISCOSITY DATA OF WHOLE PITCH AND ACETONE-SOLUBLE FRACTION

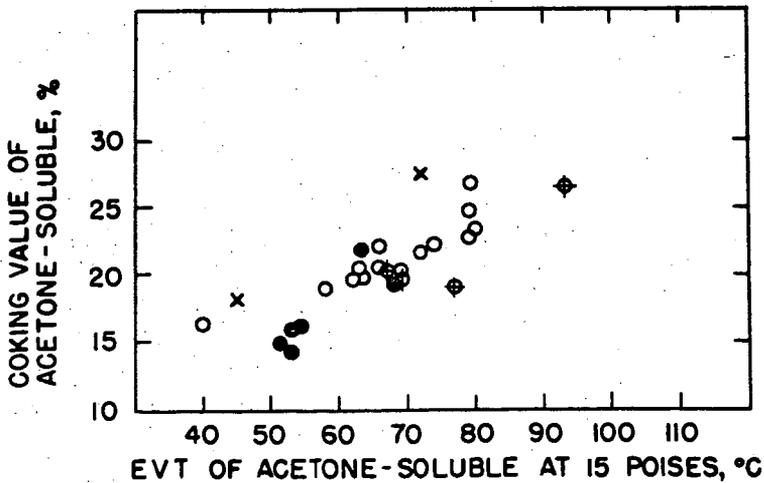


FIGURE 3

RELATIONSHIP OF VISCOSITY DATA TO COKING VALUE OF ACETONE-SOLUBLE

Quinoline-Insoluble Fraction

The quinoline-insoluble fraction is a black, very fine powder. Upon heating it does not show any sign of melting or fusing; it remains practically unchanged in appearance even when heated to 500°C. Its coking value is very high (over 95%), and shows no significant variation for the different pitches. These characteristics would suggest an almost inert material if it were not for its carbon-hydrogen ratio which varies considerably; this constitutes an interesting property which permits significant comparisons between the various pitches. For instance, the carbon-hydrogen ratio of the quinoline-insoluble of all straight-distilled pitches except one are above, or close to, 4.0; the low carbon-hydrogen of the exception (I-1) might well reflect a significant variation in the production and possibly processing of the tar; at the time this sample was produced, pitches from the same source were not considered satisfactory for carbon electrode manufacture in actual plant operation. On the other hand, for straight-distilled pitches which have been subjected to some thermal treatment such as samples C-5, A-3, and C-6, the carbon-hydrogen of the quinoline-insoluble shows a large decrease. This is probably the result of transformation of part of the quinoline-soluble, acetone-insoluble fraction into a type of quinoline-insoluble having a lower carbon-hydrogen ratio than the normal quinoline-insoluble of straight-distilled pitches. The same applies to cut-back binders prepared from heat-treated, high-melting pitches; thus the variation in carbon-hydrogen of the quinoline-insoluble can be very useful in differentiating types of pitches. It can also be observed from Table 3 that density of quinoline-insoluble fraction, is higher for straight-distilled pitches than for treated or cut-back pitches, and follows well carbon-hydrogen ratio with one exception, No. I-4; no explanation can be offered for this apparently abnormal result. This relationship between density and carbon-hydrogen ratio is much better defined for the quinoline-insoluble fraction than for the other two fractions or the whole binder.

Evidence of the presence of different types of quinoline-insoluble particles was found from microscopic examination of quinoline-insoluble fractions from different types of pitches. It was observed that the quinoline-insoluble of straight-distilled pitches consists of very fine particles, of the order of one micron, while in heat-treated and cut-back pitches the insoluble is a mixture of very fine particles and of particles of ten microns and larger; the shape of the particles is also different.

Relationship to Pitch Quality

Although it is logical to assume that fraction characteristics must have some bearing on pitch quality, no significant relationship could be established between any single characteristic and compressive strength of test electrodes which was taken as quality criterion in the investigation described herein. The only fraction which showed some promise was the quinoline-insoluble.

Examination of compressive strength and per cent quinoline-insoluble for straight-distilled pitches (see Tables 2 and 3) indicates a definite trend for higher compressive strengths to be associated with higher quinoline-insoluble contents. However, this does not hold if we examine the different types of pitch together. For instance, cut-back pitch A-5 has the highest quinoline-insoluble of all pitches and yet its corresponding compressive strength is by far the lowest. This is not altogether unexpected, since it can be easily visualized that there must be a limit to the amount of quinoline-insoluble which can be tolerated in a binder. However, this limit seems to vary for different types of pitches; for instance, straight-distilled pitch D-1 contains only a few per cent less quinoline-insoluble than cut-back pitch A-5 and yet its compressive strength is much higher. This might be explained by the large difference in carbon-hydrogen ratio of their respective quinoline-insoluble fraction, 4.3 as compared to 2.5.

It can also be visualized that there exists an optimum percentage for the quinoline-insoluble fraction. Out of mere curiosity compressive strength versus per cent quinoline-insoluble was plotted for approximately 175 pitch samples of different types and from different sources. The curve showed a maximum for compressive strength at approximately 14% quinoline-insoluble; this is roughly the quinoline-insoluble content of most of the best straight-distilled pitches shown in Table 3.

From all these observations made on the quinoline-insoluble fraction, it can be said with a reasonable degree of confidence that this fraction is of some importance in the performance of a pitch as binder. As mentioned earlier, its concentration alone is of little use if pitches of different types are considered. However, by a suitable combination of the amount of the quinoline-insoluble fraction and its carbon-hydrogen ratio and by assuming an optimum percentage - let us say 14% - it might be possible to arrive at a factor which, along with other characteristics of pitch or pitch fractions such as viscosity and coking value, might prove valuable for pitch characterization.

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LITERATURE REFERENCES

- (1) Wood, L. J., and Phillips, G., J. Appl. Chem. 5, 326 (1955).
- (2) Mallison, H., Bitumen, Asphalte, Teere, Peche, 7, 265 (1956).
- (3) Franck, M. G., Brennstoffchemie, 36, 12 (1955).
- (4) Lissner, A., and Schäfer, H. G., J. Prakt. Chemie, 1, 230 (1955).