

INFRARED SPECTROSCOPY AS A MEANS FOR EVALUATING
PITCHES FOR USE AS BINDERS IN THE PREPARATION OF
ELECTRODES FOR THE ALUMINIUM INDUSTRY. D. S. Montgomery
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The infrared absorption spectra of 28 coal tar and petroleum pitches were measured to discover the factors responsible for the quality of pitch when used as a binder in the manufacture of electrodes for the aluminium industry. The good pitches whether derived from coal or petroleum were associated with a high background absorption, and the poor pitches were associated with large proportions of CH_2 and CH_3 groups. Coal tar pitch quality improved with an increase in aromaticity of the type which gives rise to absorption bands at 6.25 and 11.4μ , and a decrease in the hydroaromatic structure associated with the 6.95μ band. Among the petroleum pitches the background absorption was as satisfactory a measure of pitch quality as the absorption at 6.25μ .

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By

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INTRODUCTION

The perfection that has been achieved in the development of instruments for measuring infrared absorption has enormously extended the use of this physical property for characterizing substances which cannot be obtained in crystalline form. Coals and pitches have recently been studied by this technique to secure information relating to the chemical structure of these complex substances (1) (2). This type of structural information should be capable of giving an insight into the reasons for the differences in behaviour of different pitches which have hitherto been difficult to explain. The following work was undertaken to see if infrared spectroscopy was capable of revealing the structural features in a pitch which are responsible for its capacity to act as a binder of petroleum coke in the manufacture of electrodes used in the aluminium industry.

Before discussing the infrared spectra in detail it may be helpful to review briefly some of the properties of commercial pitches. The pitch which is used to bind together the petroleum coke aggregate on carbonization is itself composed of a solid and a liquid phase. The solid phase consists of coke dust and high molecular weight hydrocarbons with a low hydrogen to carbon ratio which together make up what is known as the quinoline insoluble portion of the pitch. The balance of the pitch may be composed of a very wide variety of hydrocarbons and hetero compounds, but both these phases play an important part in determining the quality of the bond. On heating the coke aggregate and pitch binder, a portion of the binder is volatilized during the baking process. The portion of the binder that distills out not only makes no contribution to the bond, but creates undesirable porosity and cracks in the process of disengaging itself. For this reason a very small amount of volatile material and a high pitch coke yield have been considered as important criteria of pitch

binder quality (3). However the coke dust and other quinoline insoluble components in pitch are by themselves incapable of making a good bond owing to the lack of mobility that is necessary to wet the petroleum coke surfaces and to form a link on carbonization.

Infrared spectroscopy could not be expected to distinguish between the coke dust, consisting of amorphous and graphitic carbon, and the high molecular weight hydrocarbons which comprise the quinoline insoluble fraction, but it might give some indication of the total quantity of this class of structure that is present due to the intense continuous background absorption that is characteristic of this class of substance. On the other hand it was expected that the contribution which infrared absorption spectroscopy would make would be in the estimation of the quantity and type of aliphatic alicyclic and aromatic material present which in turn would determine the quantity of gas liberated and the amount of order in the carbon frame work produced on carbonization. Presumably a higher concentration of large fused aromatic clusters would lead to a larger quantity of graphitic structure on carbonization.

The attempts of L. P. Charette and G. T. Bischofberger (4) to find a simple laboratory test which would define binder quality seemed to present an unusual opportunity to conduct a parallel infrared study to test the validity of some of the assumptions just mentioned, and to see if infrared spectroscopy could reveal some new aspect of the problem of the characterization of pitch binders.

EXPERIMENTAL

The infrared absorption spectra of all the pitch samples were measured using the potassium bromide pellet technique. The potassium bromide used for this purpose was secured from the Harshaw Chemical Company. As the pitches varied considerably in tarriness no uniform method of sample preparation was suitable. To reduce the particle size of the pitches which were hard and dry a small high speed vibration mill supplied by Research and Industrial Instruments London was used. The disintegration of the pitch was accomplished in a cylindrical tool steel capsule 3/8" I.D. x 1-1/4" in length which was attached to a spring blade oscillating in a magnetic field. The charge in the capsule consisted of 0.3 g of pitch and two chromium plated steel ball bearings. To ensure reduction the sample was vibrated for two hours. The pitches which were too soft to be ground were simply weighed onto the top of the appropriate amount of

potassium bromide. The potassium bromide pellets were prepared by weighing .004 g of pitch to the nearest 0.0001 g together with the appropriate quantity of potassium bromide to make the pitch concentration 0.4 percent by weight. The mixture was then transferred to an agate mortar where enough benzene was added to cover the mixture. The mortar was subsequently covered with a watch glass and allowed to stand for a few minutes prior to being uncovered and ground to dryness. The benzene facilitated the dispersal of the pitch throughout the potassium bromide and aided the grinding and mixing operation conducted in the mortar. After grinding to dryness the mixture was transferred to a small beaker and dried to 110°C for at least one hour to remove all traces of the benzene. The final traces of moisture were removed by placing the sample in an evacuated desiccator over phosphorous pentoxide. Half a gram of the pellet mixture was then transferred to a die and pressed.

The spectrometer employed was a Perkin-Elmer Model 21 double beam instrument which recorded the absorption in percent transmission versus wavelength. To eliminate any absorption arising from the medium used to form the pellet a blank pellet was used in the reference beam.

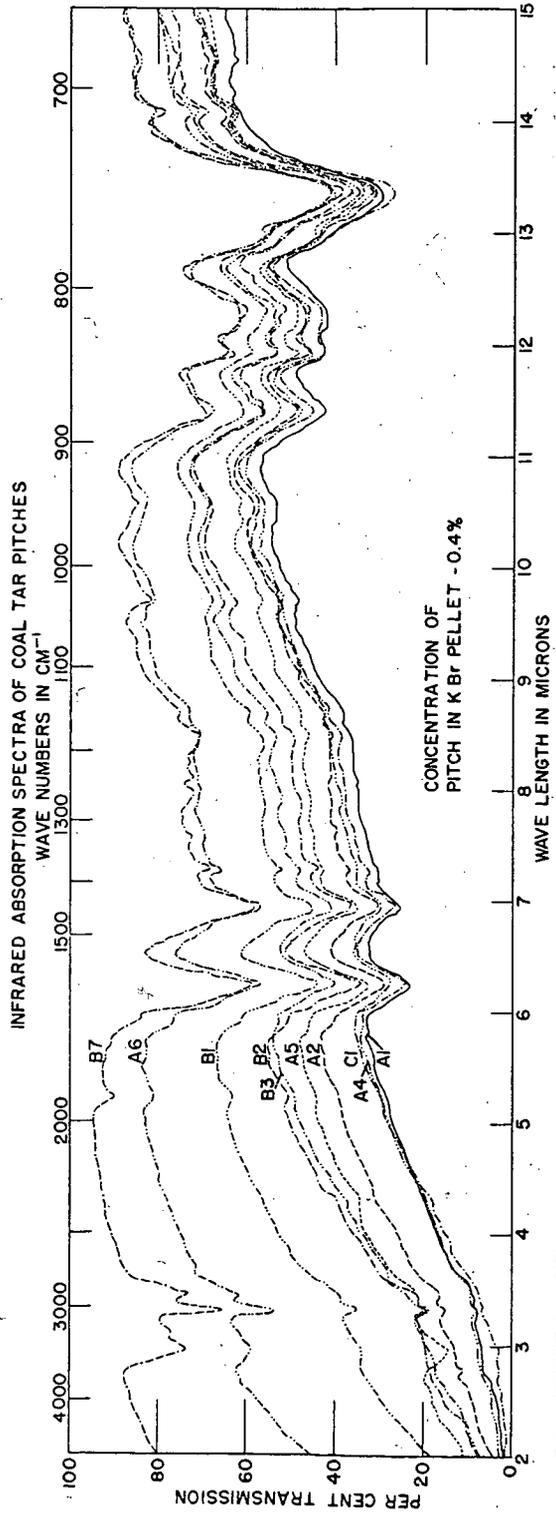
DISCUSSION OF RESULTS

On examining all 28 samples of coal tar and petroleum pitch in a cursory fashion it was evident that the coal tar pitches differed substantially from the petroleum pitches, and this suggested that the two types of pitch be discussed separately.

Absorption Spectra of Coal Tar Pitches

The coal tar pitch spectra shown in Figure I were characterized by eight significant absorption bands which were as follows:- 3.3 μ aromatic C-H 3.45 μ naphthenic and aliphatic CH, CH₂ and CH₃, 6.25 μ aromatic C=C 6.95 μ naphthenic and heterocyclic CH₂ 7.27 μ aliphatic CH₃, and the three substituted aromatic absorption bands at 11.4 12.3 and 13.35 μ . The 3.3 μ aromatic C-H band was prominent in pitches of poor quality; however as the pitch quality improved the background absorption increased and the band became so small that it was extremely difficult to measure accurately. The 3.5 μ naphthenic and aliphatic band and the 7.27 CH₃ band also suffer from the same defect in that they are readily measured when the pitches were of poor quality, but became so small in the good pitches that they could no longer be measured.

FIGURE - I



The 13.35 μ substituted aromatic absorption band was very prominent in all the coal tar pitch spectra. However, the difference in the intensity of the absorption between the best and the poorest of the pitches was much less than was found in the 11.4 μ absorption band. The standard deviation of the electrode compressive strength predicted from the absorptivity at 13.35 μ was also greater than that obtained from the predictions based upon the 11.4 μ band. These observations discouraged the use of this absorption band. The substituted aromatic absorption band between 11.95 μ and 12.5 μ appeared to be composed of a number of bands super-imposed on each other; consequently the shape of the absorption curve in this region changed considerably, and the location of the maximum was difficult to determine. As the order in which the absorption in this region placed the pitches was the same as that of the 11.4 μ absorption band which was more clearly defined, there seemed to be little merit in selecting this region for making correlations with the electrode compressive strength. These observations reduced the number of absorption bands for detailed examination to three, the 6.25 μ aromatic C=C, the 6.95 μ naphthenic or hydroaromatic CH₂ and the 11.4 μ substituted aromatic absorption band. At each of these wavelengths and at several background points the absorptivity was measured at three pitch concentrations 0.5%, 0.4% and 0.25% by weight as shown in Tables I, II and III.

To test the measure of agreement of these spectra with Beer's Law, the optical density at specific wavelengths was plotted against the sample concentration for individual pitches. Graphs showing this data for pitches A-1, A-2 and B2 are shown in Figure 2. The optical densities plotted at one wavelength for a given sample should give a straight line passing through the origin if Beer's Law is obeyed. The results seemed reasonably satisfactory with the largest deviations occurring at 2 microns where the variations in pellet quality would be expected to have the greatest effect upon the absorption spectrum due to the scatter of radiation in this region.

A cursory examination of the absorption spectra in Figure I in conjunction with the electrode compressive strength data suggested that the quality of the pitch improved with increasing background absorption. As intense background absorption was associated with the quinoline insoluble fraction this result was in accord with the view that the pitch quality improved with increasing pitch coke yield and increasing quinoline insoluble content. This background absorption was of a continuous nature upon which were superimposed the characteristic absorption bands of the atomic groups

TEST OF APPLICABILITY OF BEER'S LAW AT VARIOUS WAVELENGTHS FOR COAL TAR PITCHES

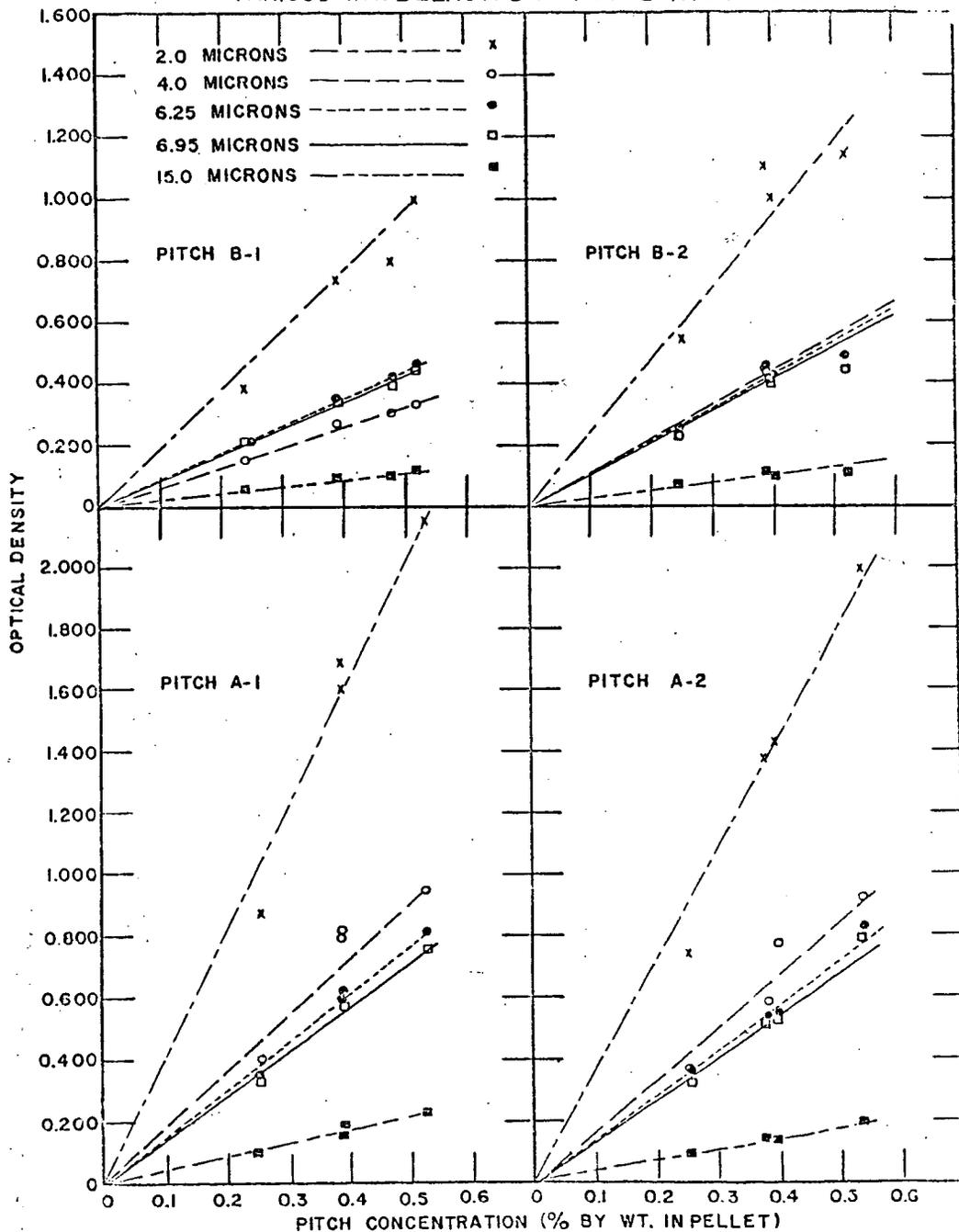


FIGURE 10

TABLE I

PER CENT TRANSMISSION AND ABSORPTIVITIES
OF COAL TAR PITCHES
(0.4% CONCENTRATION PELLETS)

Sample No.	Concentration gm. pitch per gm. pellet	Per Cent Transmission						
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	13.35 μ	15.0 μ
A-1	0.0039	2.5	16.3	23.6	25.6	42.7	29.9	64.8
C-1	0.0039	1.0	16.6	26.4	28.7	47.0	30.2	72.9
A-2	0.0040	3.7	25.0	28.3	31.5	50.0	33.0	72.7
A-4	0.0040	2.8	16.8	27.5	30.0	48.0	31.8	70.7
B-3	0.0040	8.3	37.0	39.4	41.5	57.9	33.7	78.2
B-2	0.0040	8.9	38.3	38.0	40.3	58.0	39.2	81.3
A-5	0.0039	14.0	38.1	37.8	40.3	57.7	38.1	78.0
A-6	0.0040	45.7	74.7	56.5	58.3	68.2	40.0	87.7
B-1	0.0039	18.2	53.2	44.0	45.7	61.0	40.7	80.0
B-7	0.0038	79.2	90.8	58.8	57.0	69.8	39.2	88.0

	Compressive Strength Kg/cm	Absorptivity A						
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	13.35 μ	15.0 μ
A-1	440	411	202	161	152	95.0	134	48.2
C-1	366	512	200	147	139	84.1	133	35.1
A-2	352	358	151	137	126	75.2	120	34.5
A-4	340	388	194	140	131	79.8	125	37.5
B-3	320	270	108	101	96	59.5	118	26.8
B-2	300	263	104	105	99	59.0	102	22.5
A-5	289	219	107	108	101	61.3	107	27.7
A-6	273	85	32	63	59	41.5	100	14.3
B-1	263	190	70	91	87	54.9	100	24.9
B-7	181	27	12	58	64	41.1	107	14.7

TABLE II
PER CENT TRANSMISSION AND ABSORPTIVITIES
OF COAL TAR PITCHES
(0.4% CONCENTRATION PELLETS)

Sample No.	Concentration grm. pitch per grm. pellet	Per Cent Transmission						
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	13.35 μ	15.0 μ
A-1	0.0039	2.5	16.3	23.6	25.6	42.7	29.9	64.8
C-1	0.0039	1.0	16.6	26.4	28.7	47.0	30.2	72.9
A-2	0.0040	3.7	25.0	28.3	31.5	50.0	33.0	72.7
A-4	0.0040	2.8	16.8	27.5	30.0	48.0	31.8	70.7
B-3	0.0040	8.3	37.0	39.4	41.5	57.9	33.7	78.2
B-2	0.0040	8.9	38.3	38.0	40.3	58.0	39.2	81.3
A-5	0.0039	14.0	38.1	37.8	40.3	57.7	38.1	78.0
A-6	0.0040	45.7	74.7	56.5	58.3	68.2	40.0	87.7
B-1	0.0039	18.2	53.2	44.0	45.7	61.0	40.7	80.0
B-7	0.0038	79.2	90.8	58.8	57.0	69.8	39.2	88.0

	Compressive Strength Kg/cm ²	Absorptivity A						
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	13.35 μ	15.0 μ
A-1	440	411	202	161	152	95.0	134	48.2
C-1	366	512	200	147	139	84.1	133	35.1
A-2	352	358	151	137	126	75.2	120	34.5
A-4	340	388	194	140	131	79.8	125	37.5
B-3	320	270	108	101	96	59.5	118	26.8
B-2	300	263	104	105	99	59.0	102	22.5
A-5	289	219	107	108	101	61.3	107	27.7
A-6	273	85	32	63	59	41.5	100	14.3
B-1	263	190	70	91	87	54.9	100	24.9
B-7	181	27	12	58	64	41.1	107	14.7

TABLE III

PER CENT TRANSMISSION AND ABSORPTIVITIES OF
COAL TAR PITCHES
(0.25% CONCENTRATION)

Sample No.	Concentration gm. pitch/gm. pellet	Per Cent Transmission					
		2.0	4.0	6.25	6.95	11.4	15
A-1	0.0026	13.4	39.8	44.1	46.1	62.5	79.7
C-1	0.0025	13.2	42.2	48.6	52.2	66.5	84.0
A-2	0.0026	18.0	43.3	43.1	48.5	64.7	81.0
A-4	0.0025	12.0	34.9	45.6	47.7	63.3	81.0
B-3	0.0025	26.8	57.5	60.0	60.1	72.4	87.2
B-2	0.0025	28.0	60.0	55.3	57.8	72.0	86.6
A-5	0.0025	24.5	50.0	52.1	53.7	68.3	85.2
A-6	0.0025	60.0	82.3	72.2	70.8	78.6	92.7
B-1	0.0024	41.1	71.0	61.5	62.1	74.3	87.6
B-7	0.0025	95.0	96.3	70.8	74.3	82.6	93.1

	Compressive Strength Kg/cm ²	Absorptivity, A					
		2.0	4.0	6.25	6.95	11.4	15
A-1	440	342	157	140	132	80.0	38.4
C-1	366	355	151	127	114	71.4	30.7
A-2	352	292	143	143	123	74.6	36.1
A-4	340	363	180	134	126	78.0	36.2
B-3	320	229	96	89	88	56.0	24.0
B-2	300	224	90	105	97	57.8	25.6
A-5	289	244	120	113	108	66.4	27.6
A-6	273	89	34	57	60	42.0	13.2
B-1	263	161	61	88	86	53.6	24.1
B-7	181	9	7	59	51	32.6	12.2

OH, C=C, CH₂, CH₃ and C=O. These absorption bands were thought to be more intense in the quinoline soluble portion of the pitch and a base line technique was tested to see if the background could be subtracted from the band height so that the contribution of the soluble portion of the pitch might be more clearly discerned. This did not turn out to be a fruitful approach. A more satisfactory correlation was obtained between the absorptivity at certain characteristic absorption band positions.

As a first approximation it was assumed that there was a linear dependence between the electrode compressive strength and the absorptivity at various wavelengths. The equation of correlation was obtained by the method of least squares and the standard deviations and the correlation coefficient were calculated as shown in Table IV. The standard deviations and correlation coefficients indicate that the best results are obtained with a pitch concentration of 0.4 percent at the two aromatic absorption bands occurring at 6.25 μ and 11.4 μ respectively.

The standard deviation values of the correlations between the absorptivities at the three background positions at 2, 4 and 15 μ , and the electrode compressive strength were 32.2, 28.6 and 27.3 Kg./cm² respectively. These values indicated a slight improvement in the correlation with increasing wavelength. This might be anticipated in view of the smaller contribution to the scattered radiation made by the pellet at longer wavelengths. On comparing the above standard deviations obtained at the aromatic absorption band positions 6.25 μ and 11.4 μ , which are 26.2 and 25.5 kg./cm², there is a suggestion that this improvement in standard deviation is due to the improved correlation between the background absorption and the electrode compressive strength at longer wavelength. On the other hand the poor correlation between the electrode compressive strength (E. C. S.) and the absorption at 13.35 μ suggest strongly that the chemical structure giving rise to this band has an undesirable influence upon the E. C. S.

In Table V are shown the results obtained from the correlation of the absorptivities at more than one wavelength with the E. C. S. In all the correlations it has been assumed that the E. C. S. could be expressed as a linear combination of the absorptivities at various wavelengths. This can at best only be considered to be a first approximation. The best correlation giving the lowest value of the standard deviation (23.6 kg./cm²), was obtained between the E. C. S. and the absorptivities at the 6.95 μ hydroaromatic CH₂ band and the 11.4 μ aromatic absorption band. The next best correlation was obtained between the absorptivities at the 6.95 μ hydroaromatic band and the 6.25 μ aromatic band. Both these correlations were superior to those which only involved aromatic absorption bands such as the 6.25 and the 11.4 μ bands. The correlation between these two absorption bands and the E. C. S.

TABLE IV

CORRELATION OF THE E. C. S. WITH INFRA-RED
ABSORPTIVITIES OF COAL TAR
PITCHES

Wavelength Correlated	Pellet Conc. %	Equation of Correlation *	Standard Deviation	Correlation Coefficient
2 μ	0.5	$y=0.506x + 191$	25.6	0.92
	0.4	$y=0.404x + 202$	32.2	0.872
	0.25	$y=0.53 x + 191$	30.7	0.885
4 μ	0.5	$y=0.935x + 210$	30.7	0.883
	0.4	$y=0.92 x + 204$	28.6	0.903
	0.25	$y=1.04 x + 204$	34.4	0.852
6.25 μ	0.5	$y=1.64 x + 140$	32.0	0.874
	0.4	$y=1.83 x + 110$	26.2	0.916
	0.25	$y=1.82 x + 120$	37.0	0.829
6.95 μ	0.5	$y=1.87 x + 122$	32.1	0.874
	0.4	$y=2.01 x + 101$	28.5	0.901
	0.25	$y=2.19 x + 97$	32.9	0.867
11.4 μ	0.5	$y=3.13 x + 109$	30.7	0.883
	0.4	$y=3.59 x + 79$	25.5	0.925
	0.25	$y=3.92 x + 73$	30.8	0.886
13.35 μ	0.5	$y=3.20 x - 49$	40.8	0.787
	0.4	$y=4.23 x - 172$	39.3	0.802
15 μ	0.5	$y=5.49 x + 182$	30.6	0.898
	0.4	$y=6.03 x + 140$	27.3	0.910
	0.25	$y=6.6 x + 136$	33.7	0.860

* y = Electrode Compressive Strength in Kg/ cm².
 x = Absorptivity A at Wavelength Indicated.

TABLE V

MULTIPLE CORRELATIONS OF E. C. S. WITH INFRA-RED
ABSORPTIVITIES OF COAL TAR PITCHES

Wavelength Correlated	Pellet Conc. %	Equation of Correlation *	Standard Deviation
2 μ and 15 μ	0.5	$y = 0.37 x_1 + 1.61x_2 + 211$	24.8
	0.4	$y = 0.160x_1 + 4.06x_2 + 152$	24.7
4 μ and 15 μ	0.5	$y = 0.84 x_1 + 0.50x_2 + 208$	31.8
	0.4	$y = 0.425x_1 + 3.44x_2 + 174$	25.4
6.25 and 6.95 μ	0.5	$y = 1.38 x_1 + 0.31x_2 + 136$	32.0
	0.4	$y = 5.53 x_1 - 4.16x_2 + 136$	23.9
6.25 and 11.4 μ	0.4	$y = 1.26 x_1 + 1.00x_2 + 109$	25.7
6.95 and 11.4 μ	0.4	$y = 4.52 x_1 + 11.4 x_2 + 46$	23.6
4 μ , 15 μ , 6.25 μ and 6.95 μ	0.4	$y = 0.515x_1 + 4.175x_2 + 1.060x_3$ $-1.631x_4 + 186$	23.9

* y = Electrode compressive strength; x_1, x_2, x_3, x_4 are the absorptivities measured at the wavelengths recorded in the first column in order of their presentation.

was slightly inferior to that obtained when using the absorption at the two background positions at 4 and 15 μ . From this result it was inferred that within this group of coal tar pitches the background absorption and the absorption at 6.25 and 11.4 μ were probably related.

Using the 0.4 percent concentration pellets which give the lowest standard deviations the multiple correlations involving the absorptivities at 6.25 with 6.95 μ and 6.95 with 11.4 μ it was noted that the coefficient of the 6.95 μ absorptivity is negative while the others are both positive. From this it can be concluded that the presence of hydroaromatic hydrogen atoms responsible for the 6.95 μ absorption tend to reduce pitch binder quality while the group causing absorption at 6.25 and 11.4 μ tend to improve pitch quality.

To summarize the findings up to this point, aromaticity associated with isolated benzene rings giving rise to a 3.3 μ band or substituted benzene rings yielding a 13.29 μ band are undesirable aromatic structures. The presence of hydroaromatic rings associated with absorption at 6.95 μ also reduce pitch binder quality. The chemical structures associated with absorption at 6.25 μ and 11.4 μ are the preferred aromatic structures.

The  absorption band at 11.4 μ is considered to be due to structures of the type  and the 12.3 μ band is interpreted as being due to the structure  that is to say two adjacent hydrogenations on a tetra substituted benzene ring, while the 13.35 μ band is due to ortho substitution on the benzene ring . A prominent absorption band in the 11.4 μ region implies a large number of condensed aromatic platelets. The observation that the background absorption increased with increasing absorption in the 11.4 μ region is consistent with what might be expected on increasing the number of platelets and the number of stacks of platelets. It was therefore inferred from the relation between the electrode compressive strength and the background absorption as well as the 11.4 μ absorption band, that the basic requirement for a satisfactory coal tar pitch binder was that a large proportion of the carbon atoms must be involved in highly condensed aromatic platelets.

The estimation of the E. C. S. from infrared spectroscopy appears to be somewhat less satisfactory than the method devised by Charette (4) as the standard deviation reported for both petroleum and coal tar pitches was 19 kg./cm², whereas the lowest value of the standard deviation obtained from the correlation of the infrared absorption band intensities was 23.6 kg./cm². This value will be recalled only applied to the coal tar pitches.

On examining a "cut back pitch" which possessed an intense background absorption, erroneous values were predicted for the E. C. S. The reason for this discrepancy was thought to be due to the fact that the low molecular weight solvent used to dilute the pitch contained undesirable aromatic structures whose absorption bands were obscured by the intense background.

Absorption Spectra of Petroleum Pitches

The infrared absorption spectra of the petroleum pitches are shown in Figure (3) and Tables VI. Much greater variations were encountered in these pitches than among the coal tar pitch spectra. The electrode compressive strength again appeared to be closely linked with the background absorption, but certain chemical structural groups appeared to have greater influence upon the E. C. S. than observed in the coal tar pitches. The petroleum pitches appeared to fall into roughly two classes, those pitches which possess an E. C. S. of 225 or less which transmit approximately 70 percent of the radiation at 4.0μ and those which have a much higher background absorption in this region. The pitches possessing an E. C. S. of 225 or less may be readily determined by visual inspection of the absorption curve. These pitches all possess a weak aromatic CH band at 3.3μ in relation to a strong aliphatic CH band at 3.45μ , a low background absorption in the 4.0μ region, and a relatively strong aliphatic CH_2 band at 7.25μ . The absorption band at 6.95μ , which was found to be common to all the coal tar pitches, was found to shift to 6.85μ in the petroleum pitches as the E. C. S. decreased. This shift in absorption spectrum was interpreted as being due to the increase in aliphatic CH_2 groups. On the other hand the better pitches possess an aromatic CH band of greater intensity than the aliphatic 3.45μ band. Also the background absorption in the 4.0μ region was relatively high.

Calculations were made following the procedure adopted for the coal tar pitches. Correlations were made between the E. C. S. and the absorptivity at 2μ , 6.25μ and 11.4μ and 15μ because of the success of this technique with the coal tar pitches and the undesirability of having too many special treatments for different classes of pitch. The correlation equations relating to the E. C. S. and the absorptivity at each of the above wavelengths gave the following standard deviations 31.7, 32.4, 40.5, 34.1, 33.2 kg./cm^2 as shown in Table VII. Many of the standard deviations exceed the values obtained with coal tar pitches at similar wavelengths. The petroleum pitches differed from those derived from coal in that the correlation between the absorptivity at the 6.25μ aromatic band and the E. C. S. was not significantly better than obtained at the 2μ background position. The implication was that the magnitude of the E. C. S. was not as closely related to the aromaticity in the petroleum pitches as measured by the absorption at

TABLE VI

PER CENT TRANSMISSION AND ABSORPTIVITY OF
PETROLEUM PITCHES
(0.4% CONCENTRATION)

Sample No.	Concentration gm. pitch/gm. pellet	Per Cent Transmission					
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	15.0 μ
D-1	0.0041						34.3
F-1	0.0038	9.2	23.1	26.0	26.0	44.3	67.5
G-1	0.0040	36.4	69.9	53.3	49.9	57.1	87.0
H-1	0.0040	43.0	76.0	55.4	55.8	67.2	87.0
F-2	0.0040	14.0	41.4	43.9	44.7	60.0	82.8
D-2	0.0040	72.5	89.7	60.4	51.0	72.0	91.2
D-3	0.0040	80.0	91.9	61.8	52.0	73.9	90.2
E-2	0.0040	77.7	91.7	62.8	51.0	72.7	89.6
I-1	0.0041	63.3	86.4	61.8	52.1	64.9	92.0

	Compressive Strength Kg/cm ²	Absorptivity A					
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	15.0 μ
D-1	319						11.3
F-1	315	273	167	154	154	93.2	45.0
G-1	255	111	38.8	68.2	75.5	61.0	15.0
H-1	254	91.5	30.0	64.0	63.3	43.3	15.0
F-2	242	214	95.8	89.2	87.5	55.5	20.5
D-2	210	35.0	11.8	54.8	73.0	35.5	10.0
D-3	169	24.3	9.0	52.2	71.0	32.4	11.3
E-2	167	27.5	9.5	50.5	73.0	34.5	12.0
I-1	135	48.5	15.6	51.0	69.0	45.9	8.8

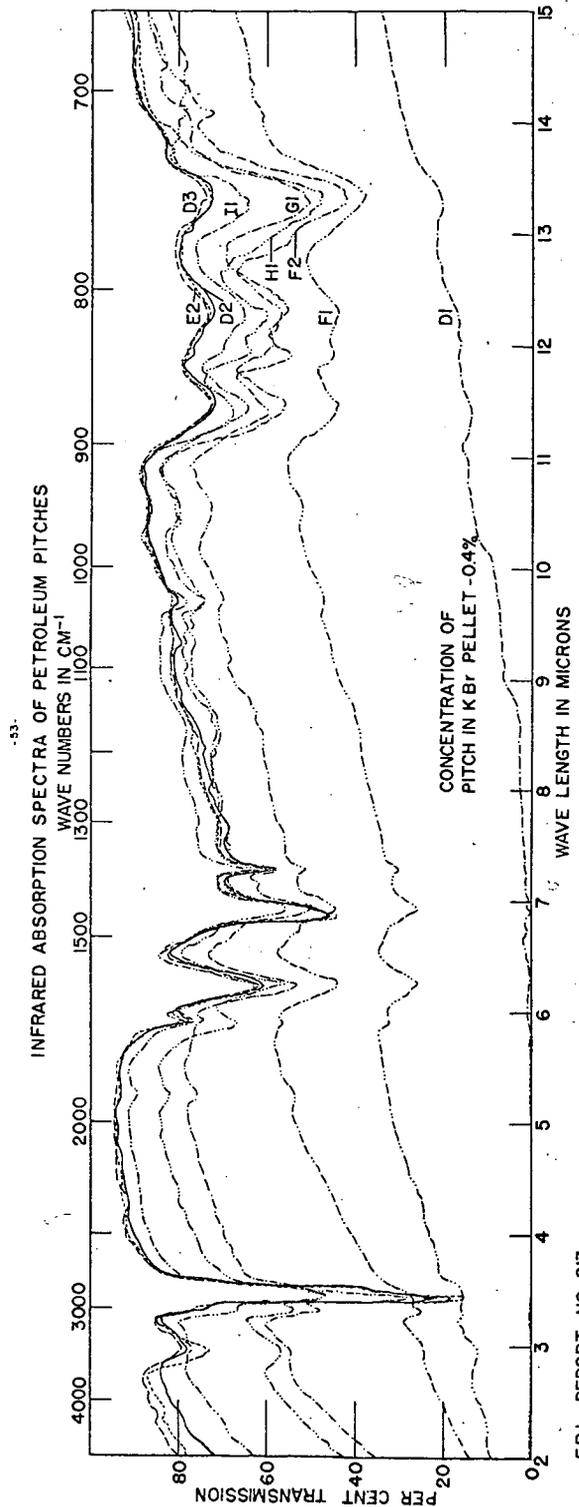
TABLE VII

CORRELATIONS OF PETROLEUM
PITCHES *

Wavelength Correlated	Pellet Conc. %	Equation of Correlation	Standard Deviation	Correlation Coefficient
2 μ	0.5	$y=0.428x + 182$	32.2	0.814
	0.4	$y=0.524x + 164$	31.7	0.821
6.25 μ	0.5	$y=1.23 x + 134$	31.5	0.821
	0.4	$y=1.37 x + 118$	32.4	0.813
6.95 μ	0.5	$y=1.28 x + 109$	39.6	0.698
	0.4	$y=1.42 x + 100$	40.5	0.701
11.4 μ	0.5	$y=2.13 x + 109$	34.9	0.774
	0.4	$y=2.33 x + 101$	34.1	0.790
15.0 μ	0.5	$y=3.49 x + 167$	34.4	0.727
	0.4	$y=3.98 x + 150$	33.2	0.796

* Pitch D-1 Not Included.

FIGURE - 3



6.25 μ or 11.4 μ . The correlation between the E.C.S. and the absorptivity at 11.4 μ was not as satisfactory as that noted in the coal tar pitches. The large background absorption suggests that large molecular aggregates are present, but there is nothing to suggest that the number of large aromatic platelets increases with increasing E.C.S. On the contrary there was a suggestion that the 13.35 μ band becomes more prominent relative to the other aromatic bands at 11.4 μ and 12.3 μ as the background absorption increases and the pitch quality improves. If the presence of carbon black is excluded this may be interpreted to mean that the high molecular weight components derived from oil tend to polymerize in a manner which does not yield a large number of large aromatic platelets, but yields a more chaotic carbon frame work associated with a slight preponderance of ortho substituted benzene rings.

To secure an insight into the effect of molecular weight upon the electrode compressive strength, a series of hard pitches prepared from Lloydminster crude oil were examined. It was previously shown that these pitches were derived from this petroleum under conditions where there was virtually no thermal cracking, and the increase in hardness was a reflection of the increase in average molecular weight resulting from the evaporation of the more volatile components. The softening point of these pitches varied from 145°F to 288°F (Ring and Ball), increasing with increasing molecular weight as may be seen in Table VIII.

The infrared absorption spectra of this series of pitches shown in Figure 4 possessed all the prominent absorption bands associated with poor pitch quality, that is to say too little aromaticity and too much aliphatic CH₂ and CH₃. This poor quality was confirmed for the measured value of the E.C.S. of pitch sample 1-5 was 73 kg./cm². While the precision obtainable at this low level of compressive strength was poor it did indicate that the test electrode was extremely weak. The background absorption from 2 to 15 μ increased with increasing molecular weight as might be expected, however the increase was quite small.

The indications from this work are that even if the molecular weight of the pitch is of approximately the right order, as indicated by the softening point 203-221°F (Ring and Ball) the quality of the pitch may be very poor. The structure of the macromolecules in the pitch appeared to play the dominant role in determining pitch quality.

FIGURE - 4

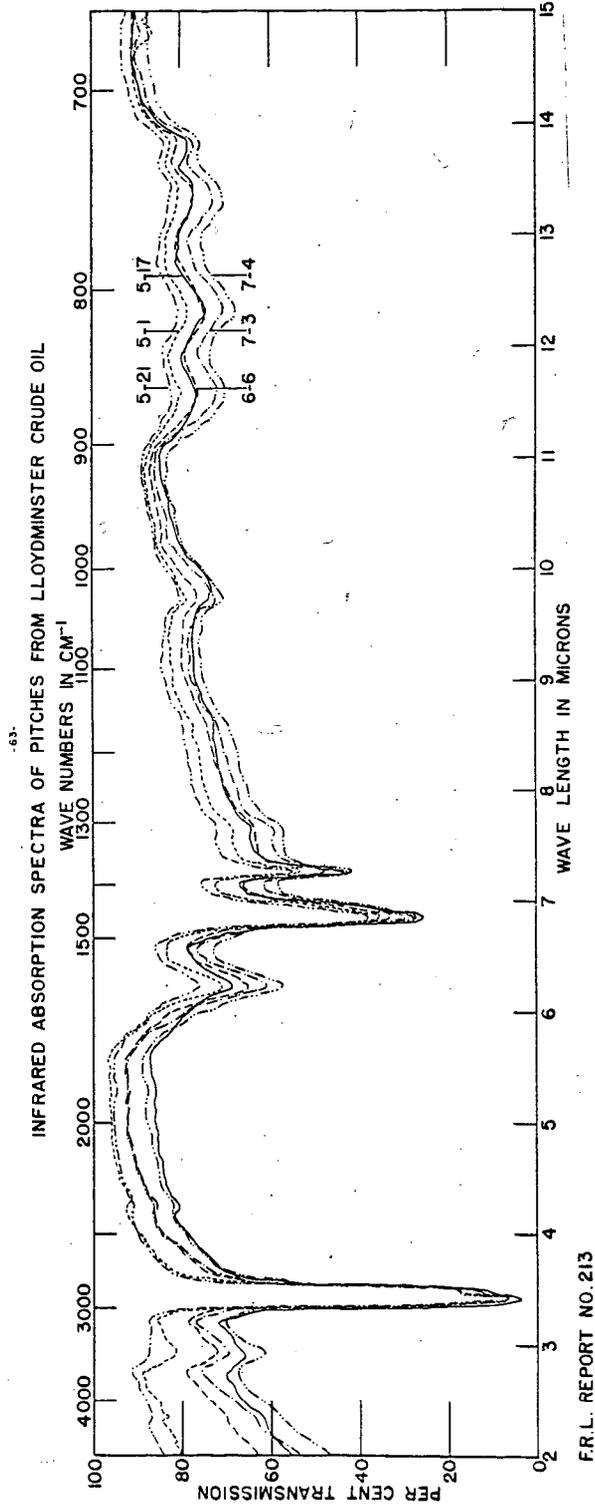


TABLE VIII

PER CENT TRANSMISSION AND ABSORPTIVITY
LLOYDMINSTER PETROLEUM PITCHES

Sample No.	Concentration gm. pitch/gm. pellet	Per Cent Transmission				
		2 μ	4 μ	6.25 μ	6.85 μ	15 μ
5-17	0.0057	50.8	78.6	68.0	25.2	92.2
5-21	0.0050	85.0	89.8	75.8	37.8	93.0
5-1	0.0055	80.6	90.0	70.7	35.4	88.0
6-6	0.0051	62.8	83.2	64.8	33.0	92.0
7-3	0.0061	53.7	83.8	60.7	27.1	90.9
7-4	0.0058	47.0	79.2	57.1	27.8	87.8

Sample No.	Softening Point °F.	Absorptivity				
		2 μ	4 μ	6.25 μ	6.85 μ	15 μ
5-17	145	51.6	18.4	29.5	105	6.3
5-21	170	14.0	9.4	24.2	84.6	6.4
5-1	197	17.1	8.4	27.5	80.2	10.2
6-6	223	39.6	15.7	37.1	94.5	7.1
7-3	252	44.3	12.6	35.6	93.0	6.9
7-4	288	56.6	17.6	42.1	95.8	9.8

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