Surface Properties of the Quinoline-Insoluble Fraction of Coal-Tar Pitch

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THE GENERAL consensus of the literature on binder materials for the production of Soderberg electrodes in the aluminum industry is that a coal-tar pitch is the preferred binder material (*4*). Studies directed toward establishing the most suitable methods for the preparation of an electrode-binder pitch from a coal tar and methods for improving the binding quality of pitches have been of considerable interest to both the producer and the consumer of electrode-binder pitch. Although compressive-strength measurement on test electrodes has been a satisfactory method of evaluating pitches for production of carbon electrodes, this method is time-consuming. It would be much more satisfactory to be able to predict electrode-binder efficacy on the basis of the chemical and physical properties of the pitch. Only then would it be possible to interpret the binding action in terms of pitch composition and perhaps to modify the pitch in a manner which would have a predictable effect on the binder action.

Charette and Bischofberger (*3*) concluded that pitch quality, as expressed by the compressive strength of test electrodes, is apparently not a function of any pitch property taken individually, but rather of a combination of properties. These investigators and others have considered correlations of compressive strength of electrodes with such properties of pitch as coking value, density, aromaticity, softening points, and distribution of fractions produced by solvent extraction.

One general method of characterizing pitches is that of solvent analysis. In one such technique, the pitch is extracted first with a paraffinic solvent, and the residue is then re-extracted successively with benzene and quinoline. Martin and Nelson (*9*) state that "in pitch binder quality, the quinoline-insoluble (Q. I.) fraction, essentially a nonfusible powder, is important."

The practical importance of the Q. I. fraction of pitch is recognized by the inclusion of a Q. I. minimum in many specifications for electrode-binder pitches. Information on the theoretical significance of the Q. I. material is rather scarce. The Q. I. material per se does not contribute directly to the binding action of the pitch (*1*), and generally it is considered as inert material which may have a beneficial effect in decreasing the effect of temperature on the viscosity of pitch (*5*). Thus, one notes in the literature a tendency to consider the Q.I. portion of pitch as a finely dispersed carbonaceous filler of questionable function in the binding action of the pitch.

Because little information could be found on the surface properties of the Q. I. fraction of pitch and because studies of the surface chemistry of carbon black have led to a better understanding of the use of this material in the rubber industry, an exploratory study of the surface properties of the Q. I. portion of pitch was made. It was hoped that this information might lead to a better understanding of the function of Q. I. material in the applications of pitch as an electrode binder.

EXPERIMENTAL

For this work, a total of nine experimental binder pitches, representing a considerable range of Q. I. content, was selected. The usual analytical data on these pitches are summarized in Table I. Pitches 1 through 6, representing a range of Q. I. from 2.4 to 13.1%, had been prepared to an approximate constant softening point of 90° C. To achieve rather extreme variation in Q. I. content, pitch A was thermally treated to produce pitch B having a very high benzene-insoluble and quinoline-insoluble content. Pitch C was produced to have a low Q. I. content by centrifugation of a quinoline suspension of the parent tar of pitch A, followed by removal of the quinoline and further distillation.

The Q. I. fractions used for this study were isolated as follows: A 100 gram portion of pitch was crushed and ground to pass a 60-mesh sieve. The pitch was then added slowly with stirring to 250 ml. of warm (70° to 90° C.) quinoline in a 600-ml. beaker. After 15 to 20 minutes at this temperature, the mixture was filtered through a Büchner funnel fitted with a Whatman No. 50 filter paper. The retained Q. I. were washed with an additional 250 ml. of warm quinoline in small portions and then with 500 ml. of benzene to remove the quinoline. After air-drying, the Q. I. were oven-dried at 110° to 115° C. for 1 hour. This method of preparation gave yields of Q. I. materials nearly equal to those obtained by the analytical procedure and reported in Table I.

Surface area was measured by the Brunauer, Emmett, and Teller method (*2*). The samples were degassed at 200° C. for 12 hours before measuring the nitrogen isotherm at 77° K.

Preparation and testing of specimen electrodes using the various pitches as binders were carried out according to the procedure of Jones, Simon, and Wilt (*7*).

RESULTS AND DISCUSSION

The data on the Q. I. fractions of the experimental pitches are summarized in Table II. For these particular samples, the surface area per gram of Q. I. tends to decrease as the

Table I. Analytical Data on Experimental Pitches

Pitch[a]	Softening Point, ° C. C.I.A.[b]	Benzene-Insoluble, Wt. %	Q. I. Wt. %	β-Resin[c]	Coking Value,[d] Wt. %	Carbon, %	Hydrogen, %	Atomic C/H Ratio
1	89.0	33.2	13.1	20.1	58.6	93.34	4.36	1.80
2	90.2	32.6	12.8	19.8	57.1	93.41	4.07	1.93
3	93.5	29.7	10.6	19.1	54.1	93.31	4.18	1.87
4	94.9	28.0	9.1	18.9	52.7	92.88	4.44	1.76
5	90.6	17.5	6.9	10.6	50.2	92.55	4.38	1.78
6	88.2	13.0	2.4	10.6	49.8	91.35	4.77	1.61
A	102.3	25.5	12.4	13.1	56.7	93.22	4.24	1.84
B	98.5	50.3	35.0	15.3	64.9	93.48	4.00	1.96
C	95.0	25.0	4.2	20.8	51.9	93.29	4.52	1.73

[a] 1. Thermal treatment of a 74° C. pitch at 380° C. for 24 hours and backblending with 9.1% of starting pitch. 2. Laboratory distillation of soft pitch from a production tar. 3. Laboratory distillation of 36.2 wt. % from a production tar. 4. Blend of 88.55 wt. % 105° C. pitch (produced by distillation of light tar at 50 mm. to 300° C.) with 11.45% of coal-tar distillate oil (boiling 230 to 270° C.). 5. A production pitch after removal of *n*-heptane–solubles. 6. Laboratory distillation of a 69° C. pitch from light tar. A. Production by plant distillation of production tar. B. Produced by thermal treatment of A to have maximum benzene-insoluble and quinoline-insoluble content. C. Produced by adding quinoline to the parent tar of A, centrifuging this mixture to remove insolubles, and then distilling.

[b] Cube-in-air method.

[c] Benzene-insoluble − Q. I. = β-resin.

[d] Determined essentially according to the Conradson carbon residue determination, ASTM D 189–46.

Table II. Data on Quinoline Insolubles

Q. I. Fraction	$\frac{\text{C.V.} - \text{Q.I.}}{\text{Q.I.}}$	Surface Area, Sq. M./G.	Surface Area per 100 G. Pitch, M^2	Carbon, %	Hydrogen, %	Atomic C/H Ratio
1	3.47	9.4	123	92.59	3.06	2.54
2	3.46	10.4	133	93.02	2.43	3.21
3	4.1	13.2	140	93.06	2.01	3.89
4	4.8	16.3	148	91.60	2.11	3.64
5	6.28	16.8	116	93.13	2.00	3.90
6	19.4	22.9	55	91.45	2.47	3.10
A	3.57	15.9	197	94.76	1.89	4.21
B	0.85	8.0	280	94.67	3.04	2.61
C	11.4	19.4	82	93.36	2.30	3.41

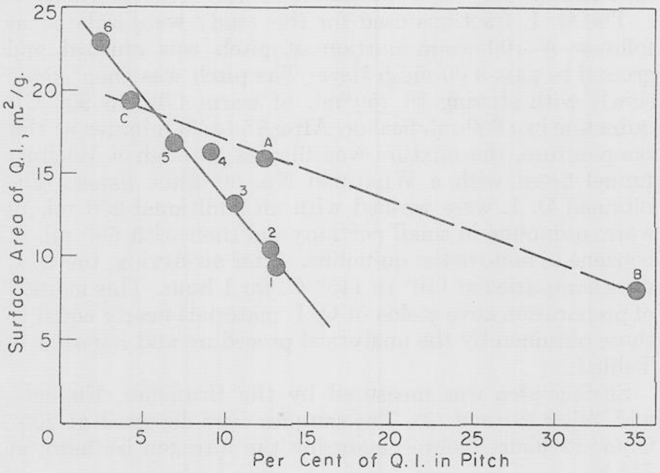


Figure 1. Q. I. content of the pitch *vs.* Q. I. surface area

amount of Q. I. in the pitch increases (Figure 1). This trend is exhibited both by pitches 1 through 6 and by the interrelated series, A, B, C, although the rate of change varies. This observation suggests that a process such as thermal treatment, which tends to increase the amount of Q. I. in the pitch, also produces an agglomeration or increase in particle size of the Q. I. material.

Thermal treatment of a pitch (A) containing 12.4% Q. I. with a surface of 15.9 square meters per gram yielded a product pitch (B) containing 35.0% Q. I., but with a surface of only 8.0 square meters per gram. When the Q. I. content was reduced to 4.2% by extraction of the parent tar with quinoline, centrifugation to remove most of the Q. I., removal of solvent, and distillation, the residual Q. I. in the pitch (C) had a surface area of 19.4 square meters per gram.

In a number of cases (such as the Q. I. from pitches 6 and 2), the Q. I. was found to be almost entirely spherical in habit (Figures 2 and 3). The average particle size is of the same order of magnitude as that anticipated from surface area measurements, with pitch 6 having the smaller average particle size and higher surface area.

Having shown that Q. I. material can differ in surface area and particle size, it was interesting to examine the surface for differences in chemical reactivity. For this purpose, the polarographic reducibility of the surface of the Q. I. material was determined by the method of Hallum and Drushel (*6*). As noted in Figure 4, the polarographic reducibility of the Q. I. appeared to be a direct function of the surface area. This relationship between polarographic reducibility and surface area was taken as an indication of the chemical uniformity of the surface of the Q. I. material. The limited number of samples examined prohibit any firm position on this indication. However, the significance of surface reducibility might be more profitably pursued in the study of Q.I.'s of the same surface area where differences in reactivity are suspected. A sample of petroleum coke of comparable surface area showed no reducibility.

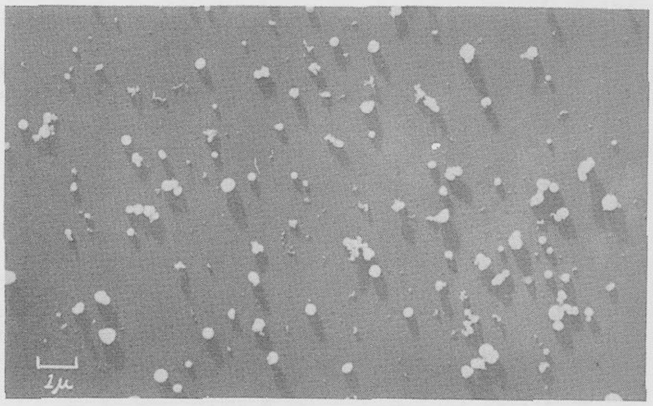


Figure 2. Photomicrograph of the Q. I. of pitch 6, illustrating a Q. I. of high surface area

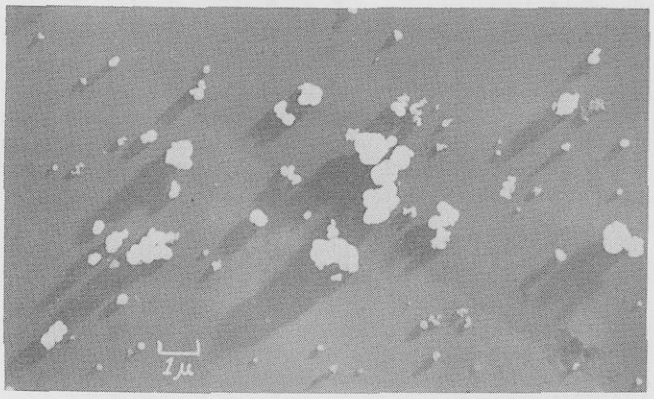


Figure 3. Photomicrograph of the Q. I. of pitch 2, illustrating a Q. I. of low surface area

Before considering the effect of the surface area of the Q. I. portion of pitches on the properties of electrodes prepared from pitches, the available data were examined for evidence of surface effects during the coking of the pitch itself. If the surface area of the Q. I. is an important factor in binding action, it seemed reasonable to anticipate some effect on the yield of coke available from the pitch.

If it is assumed that all quinoline-soluble material is

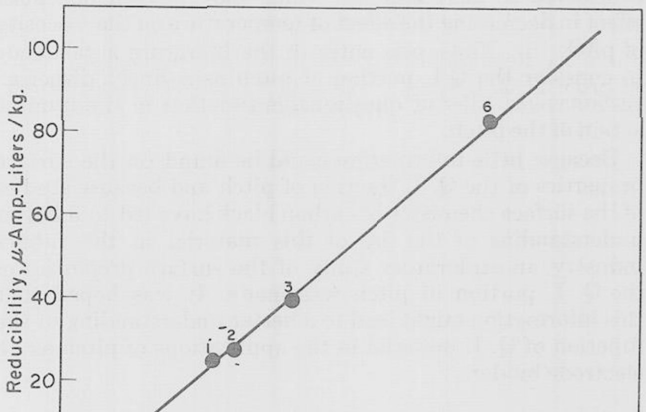


Figure 4. Relationship of the polarographic reducibility to surface area of the Q. I.

available for the formation of coke and the Q. I. is relatively unchanged during coking, a plot of the amount of new coke formed (coking value − Q. I.) per unit weight of Q. I. *vs.* the surface area per unit weight of Q. I. should give an indication of the effect of Q. I. surface area on the yield of coke. Figure 5 shows this relationship and indicates that Q. I.'s with a high surface area promote a high yield of coke per unit weight of Q.I. The variant pitches B and C, produced from A, show this same qualitative relationship. This relationship suggests that the surface of the Q.I. may function as the site of coke formation.

The usual test data for the specimen electrodes are tabulated in Table III. The apparent density, resistivity, and compressive strength of the electrodes as a function of the amount of surface available from the Q. I. in 100 grams of binder are shown in Figures 6, 7, and 8. These figures show that apparent density and compressive strength reach a maximum at about 125 to 150 square meters of surface in 100 grams of pitch, and the resistivity reaches a minmum in the same region.

Also, these figures suggest that an optimum surface area or particle size of Q. I. exists which permits the formation of electrodes with optimum properties. The results are quite similar to those of Krylov and others, who found in their studies of the free-carbon content of pitch that at about 16% free carbon the density and compressive strength of electrodes pass through a maximum and resistivity reaches a minimum (*8*).

CONCLUSIONS

Although the Q. I. fraction of an electrode-binder pitch reportedly has no binding action in itself, it is credited with being important to electrode-binder efficacy of the pitch. The actual role of the Q. I., however, remains vague. It was therefore the purpose of this study to examine the surface properties of Q. I.'s of several experimental pitches in the hope that some information might thus be obtained which would be helpful in elucidating the role of the Q. I. On the basis of nine different pitches, the Q.I.'s of which varied, irregularly, from 2.4 to 35%, the following effects were observed:

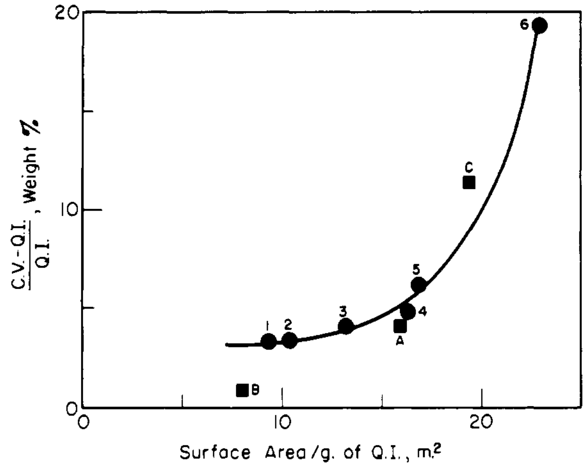
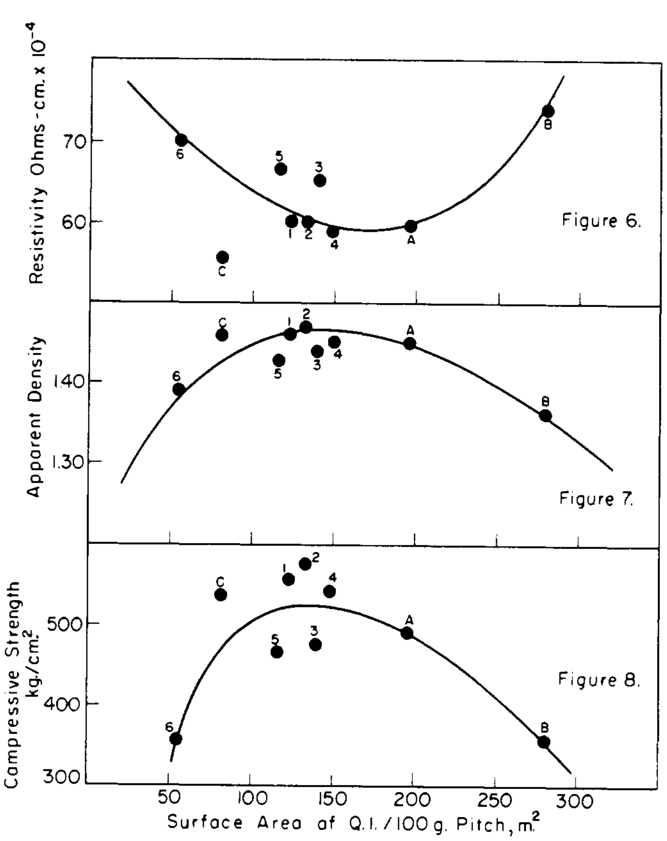


Figure 5. Relationship between the yield of new coking value per gram of Q. I. (C. V. − Q. I./Q. I.) and the surface area per gram of the Q. I.

Table III. Test Data on Specimen Electrodes Prepared from Experimental Pitches

Pitch	Apparent Density, G./Cc.	Resistivity, Ohm-Cm.	Compressive Strength, Kg./Sq. Cm.
1	1.46	60.1×10^{-4}	557
2	1.47	60.3×10^{-4}	577
3	1.44	65.2×10^{-4}	472
4	1.45	59.0×10^{-4}	541
5	1.43	66.8×10^{-4}	468
6	1.39	70.1×10^{-4}	357
A	1.45	59.6×10^{-4}	490
B	1.36	74.0×10^{-4}	356
C	1.46	55.5×10^{-4}	538



Figures 6. to 8. Relationships among the resistivity, apparent density, and compressive strength of test electrodes prepared from each of the experimental pitches and the surface area of the Q.I. in 100 g. of the respective pitch

1. The larger the percentage of Q. I. content of a pitch, the smaller is the surface area per gram of Q. I., and hence the larger is the average particle size. This is qualitatively borne out by electron photomicroscopy.
2. The polarographic reducibility of the Q. I. appears to be directly related to surface area, an indication that the reactivity of the surface is essentially uniform.
3. The yield of new coking value per gram of Q. I., $\frac{C.V. - Q.I.}{Q.I.}$, is directly related to the surface area per gram of Q. I. This suggests that the Q. I. surface may serve as the site of new coke formation.
4. Evaluation of test electrodes prepared from these pitches indicates that there may be an optimum range of interfacial area between the Q. I. and the remainder of the pitch. In this range, the apparent density and compressive strength of the electrodes pass through a maximum and the resistivity through a minimum.

This study has been an examination of some of the parameters of the Q. I. which might shed light on its function in the pitch. It is hoped that these preliminary, generalized trends of some Q. I. properties will be useful to investigators who are currently exploring this field.

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A Laboratory Evaluation of Pitch Binders Using Compressive Strength of Test Electrodes

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A MAJOR USE FOR coal-tar pitch is as an electrode binder for Soderberg electrodes in the aluminum industry. One of the methods for determining whether a pitch is of suitable quality for use in production electrodes is to prepare and bake a test electrode using the pitch and a standard calcined petroleum coke, and then to determine the compressive strength and other physical characteristics of the electrode. However, there appears to be very little published on methods for preparing and testing carbon electrodes. One method (*5*) involves the preparation of relatively large electrodes (approximately 6 inches in diameter and 8.5 inches long), which requires large and expensive equipment for mixing and baking. An improvement of this method was developed so that readily available laboratory-size equipment could be used to prepare a batch of four test electrodes, 1.25 inches in diameter and 4 inches long.

This procedure was used in a program to relate various properties of a pitch to its electrode-binder characteristics.

EXPERIMENTAL

Preparation of Test Electrodes. The electrode paste, which is made from a mixture of the pitch and petroleum coke particles (Table I), is baked in a graphite mold. The molds are prepared from graphite rods 1-5/8 inches in diameter (National Carbon Co., Type AGX or AJX) which are cut into pieces 5 inches long. A hole 1-1/4 inches in diameter is drilled throughout the length of each piece. The drilled hole is reamed with a tapered reamer so that the inside diameter of the one end is 1-9/32 inches and the other end is 1-1/4 inches. This taper permits easier removal of the electrode after baking. The inside of the mold is then lined by gluing in a layer of Kraft wrapping paper. A template is then used to aid in drilling 96 vent holes 0.076 inch in diameter (No. 47 drill) through the graphite shell of the mold (Figure 1). If desired, the molds can be re-used several times by cleaning, relining, and punching vent holes in the liner.

The pitch is broken into small pieces and placed in a steam-jacketed, 1-quart sigma blade mixer (Charles Ross and Son, Brooklyn, N. Y.), where it is melted at a temperature which is approximately 30° to 40° C. above the softening point. For pitches with a softening point of about 90° C., 10 minutes at a temperature of 130° C. is usually sufficient. The mixer blades are placed in motion, and the previously heated (120° to 130° C.) petroleum coke particles are added, starting with the coarsest fraction and allowing 5 minutes of mixing between the addition of fractions. After the last fraction is added, the paste is mixed for 5 minutes.

While the paste is being mixed, four of the graphite molds are heated to about 120° C. using an electrical beaker mantle in which the molds rest on a flat graphite plate. The molds are gradually filled in turn with small portions of paste taken directly from the mixer using a metal rod as a tamper to achieve a uniform density. The paste behaves as a heavy fluid after it has been evenly packed in the mold. Each is filled to within 1/2 inch of the top.

The filled molds are then allowed to cool until the paste forms a hard solid. Two grams of petroleum coke particles, 200 to 325 mesh, are placed on top of the solidified paste.

Table I. Composition of Paste Used in Preparing Test Electrodes

Component	Weight, G.	Wt. %
Pitch	262.8	31.1
Calcined petroleum coke		
10 to 30 mesh[a]	116.7	13.8
30 to 50 mesh	93.4	11.0
50 to 100 mesh	110.9	13.1
100 to 200 mesh	75.9	9.0
200 to 325 mesh	58.4	6.9
325 to pan	128.2	15.1
Total	846.3	100.0

[a] U. S. Standard sieve sizes.

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