THE RELATIONSHIP OF PITCH PROPERTIES TO ANODE PROPERTIES

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Introduction

The aim of this report is to provide help in appraising a pitch for suitability as binder in the anodes of the alumina reduction plants. The information was gained from testing over 148 pitches from 21 producers. Commercially available and experimental petroleum oil, gas, asphalt, regular and low-temperature coal tar pitches were included.

An indication of the suitability of a pitch as binder is obtained by using as an index the properties of baked electrodes made in the laboratory with the test pitch. The electrodes are prepared using controlled conditions designed to maintain all variables as constant as possible other than the pitch being appraised. The laboratory techniques used produce electrode specimens that have the same level of values for the properties of apparent density, electrical resistivity, total porosity and crushing strength as those produced in the plant from the same materials.

This report (1) is based on the application of this technique to laboratory specimens of Soderberg composition. It furnishes some comparisons of the resulting properties to those of the anodes in the plants. (2) It gives the correlation found between the properties of the laboratory specimens and the analysis of the binder pitch. (3) It furnishes the percentage influence found for the measured pitch properties on variations in the properties of the laboratory-prepared carbon. (4) It provides equations which can be used to predict these properties of the laboratory specimens from the analysis of the binder pitch. Only the common determinations of softening point, coking value, components insoluble in benzene and quinoline, specific gravity and distillate fractions are required. The difference between the predicted and the measured physical properties are generally within the precision of the methods for measuring the properties. These equations can be used as guides by laboratories without facilities for preparing carbon anode specimens, by people with limited experience in evaluating pitches, and by pitch manufacturers in developing binder pitches.

Experimental Results

Comparison of Properties of Laboratory Specimens with Those of Plant Anodes

Table I provides a comparison of the properties of baked carbon of Soderberg composition made of the same materials in the laboratory and in the reduction plant. This one comparison given as an example has been confirmed many times. This agreement between these properties of laboratory specimens and baked plant anodes greatly shortens the time required for a pitch appraisal in terms of these properties-- from soon after the arrival of the pitch sample in the laboratory, contrasted with six weeks or more after using the trial pitch in the Soderberg plant.

Correlation Between Pitch Properties and Properties of Laboratory Specimens.

Having established a technique for duplicating plant anode properties in the laboratory, it was used to determine the correlation between these properties and the properties of the pitch. During the period of 1941-1954, a plant laboratory found the following relationships. With few exceptions, as the softening point, coking value, benzene insoluble, quinoline insoluble, and specific gravity of the pitch increased, the values for anode properties of apparent density and crushing strength also increased. This was accompanied by a decrease in electrical resistivity and total porosity. These findings differed in two respects from the experience reported by some laboratories during this period. The difference between the amount of benzene and quinoline insoluble components, commonly designated as "beta resins", was not found to have a pronounced correlation with these anode properties. Of special interest was the finding that the half of the specimens which had the highest apparent density and crushing strength and the lowest electrical resistivity and total porosity were made with pitches which had more than 10% of components insoluble in quinoline. At that time some had recommended that purchase specifications should restrict the quinoline insoluble content to a maximum of 10%.

Findings of the plant laboratory for a series of 28 coal tar, petroleum, and experimental pitches, submitted by nine pitch producers, are given in Figure 1. The properties of the anode specimens are arranged in order of increasing apparent density. The properties of the pitch from which each anode was made are listed directly underneath. Instead of drawing the best straight line through the plotted data points, they were connected to adjacent points to show that most of the properties of pitches which were measured are inherently interrelated and strongly affect the properties of the anodes.

This approach to the evaluation of pitches was continued by the Research Laboratory when it began operating in 1955. During a period of four years, 114 additional pitches were tested. This series also included commercial and experimental petroleum oil, gas, asphalt, regular and low-temperature coal tar pitches from domestic and foreign producers. The relationships between properties of pitches and anode specimens made with them found by the plant laboratory were confirmed. There was no indication that changes in pitch manufacturing operations nor in sources of supply changed the general relationship of the properties of pitches to laboratory specimens during the 19-year period. To determine to what extent the peaks and depressions in the plotted relationship of pitches and anodes were due to plotting different pitch types, sources of tars, and processes, separate graphs were made for pitches of one type. Figure 2 makes the comparison for nine coal tar pitches from a single vendor during a two-year period. Figure 3 shows the relationship for 12 pitches of petroleum origin. In general, the interrelation of pitch properties and their effect on the laboratory specimens was found to apply to all types of these pitches.

Another Comparison of Laboratory and Plant Experience.

Figure 2 shows a pronounced relationship of the softening point of high-temperature coal tar pitches to anode properties. Additional confirmation that laboratory experiences are translatable into plant experience is furnished in Figure 4. It contains data for plant paste made with three pitches having different softening points. Figure 4 indicates the reproducibility of sample testing and constant quality of plant paste over a three-month period, and the sensitivity of the test method to detect changes in paste induced by changes in the binder. Material used in this series was obtained from routine sampling of plant paste for quality control. It shows how changing from a binder with a softening point of 90°C to one with 110°C resulted in improvement in these properties, to the extent of shifting the range for apparent density from 1.51-1.59 to 1.55-1.65 gms./cu.cm., electrical resistivity from 58-65 to 52-61 ohms/m./sq.mm. and crushing strength from 6,200-7,500 to 6,800-9,000 lbs./sq.in.

Percentage Influence of Measured Pitch Properties on Variations in Properties of Baked Laboratory Specimens.

A multiple correlation was made to determine quantitatively the effect of each of these properties of the binder on those of the baked carbon. Data was processed from 455 specimens representing 51 pitches of all types tested over a two-year period. This series of pitches produced laboratory specimens with a range in properties of

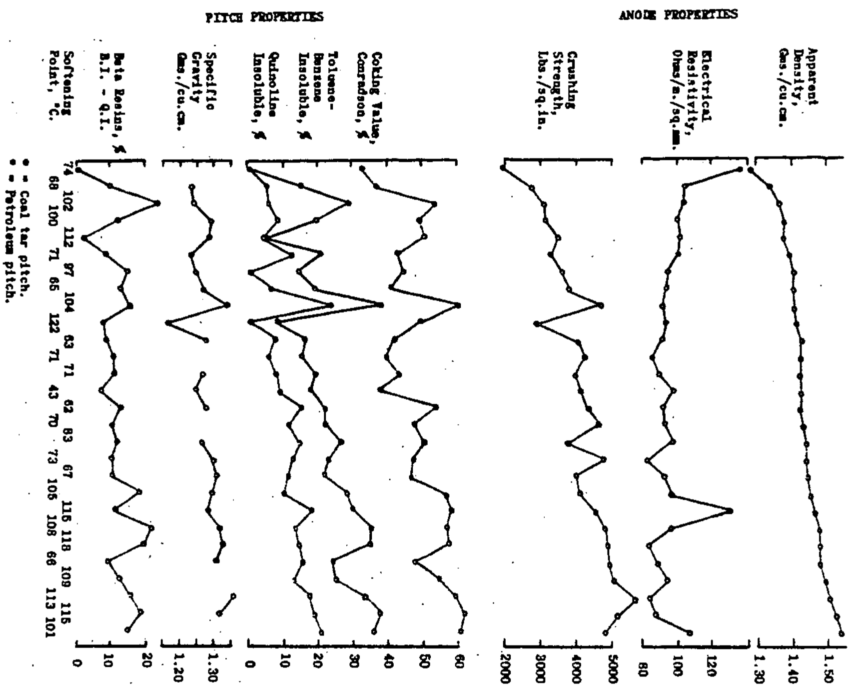

FIGURE 1. CORRELATION OF THE PROPERTIES OF LABORATORY SODERBERG SPECIMENS WITH BINDER PROPERTIES. BACKGROUND EXPERIENCE 1941-1954.

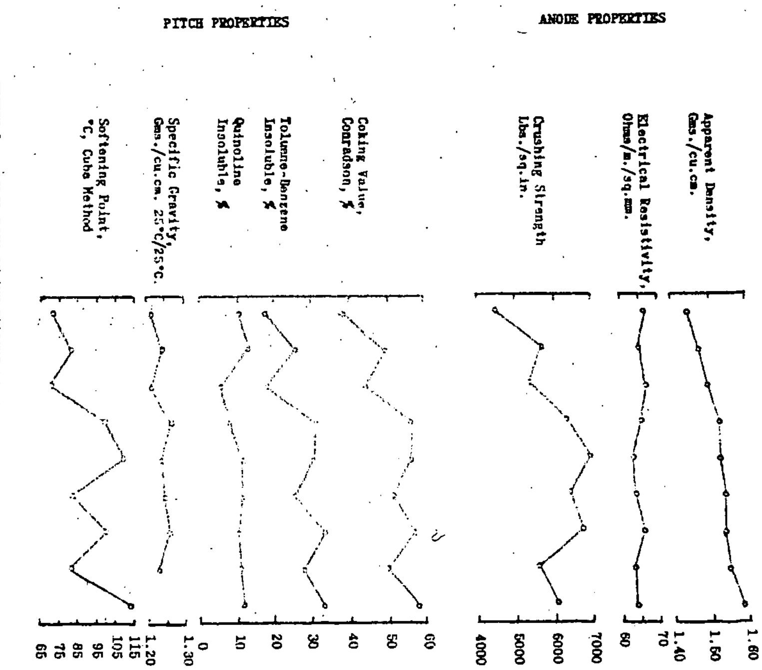

FIGURE 2. CORRELATION OF THE PROPERTIES OF LABORATORY SPECIMENS WITH BINDER PROPERTIES. HIGH TEMPERATURE COAL TAR PITCHES FROM ONE PRODUCER OVER TWO-YEAR PERIOD.

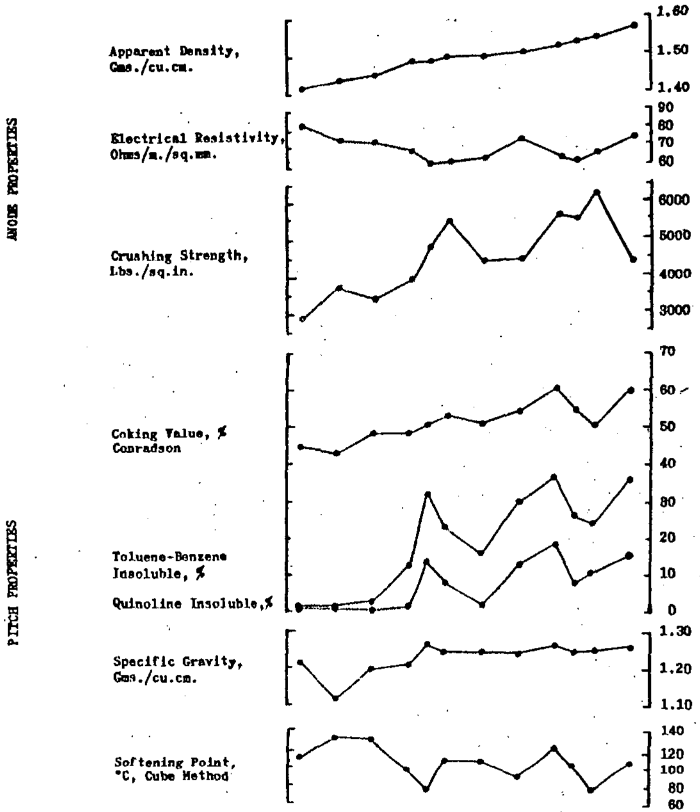

FIGURE 3. CORRELATION OF THE PROPERTIES OF LABORATORY SODERBERG SPECIMENS WITH BINDER PROPERTIES. ASPHALT, OIL, AND GAS PITCHES FROM SIX PRODUCERS.

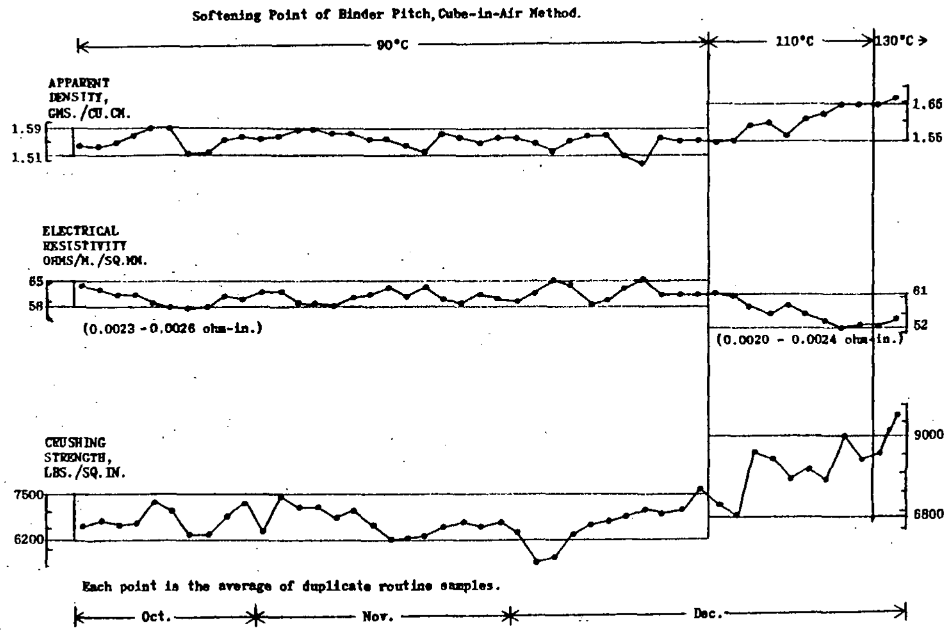

FIGURE 4. APPLICATION OF TESTS TO PLANT PASTE BAKED IN LABORATORY SHOWS REPRODUCIBILITY, SENSITIVITY, AND RELATIONSHIP TO SOFTENING POINT.

1.34 to 1.60 gms./cu.cm. apparent density, 53.3 to 80.9 ohms/m./sq.mm. electrical resistivity, and 2,450 to 7,100 lbs./sq.in. crushing strength. The percentage influence of the measured pitch properties on variations in properties of baked carbon with the constant aggregate, mixing and baking conditions is given in Table II. The multiple correlation coefficients revealed that 83.7% of the variation in apparent density, 64.8% of the variation in electrical resistivity, and 79.6% of the variation in compression strength of baked carbon under these testing conditions are accounted for by variations in the six properties measured.

The correlation of the atomic carbon to hydrogen ratio of the whole pitch to these properties of the laboratory specimens was also made. It was found that its correlation did not significantly improve the predictability of the properties over that obtained with the multiple correlation equations for the six more common determinations.

TABLE I.

COMPARISON OF PROPERTIES OF BAKED ANODES OF SODERBERG COMPOSITION MADE OF THE SAME MATERIALS BY THE LABORATORY AND BY A REDUCTION PLANT

Anode Preparation	Apparent Density Gms./cu.cm.	Electrical Resistivity, Ohms/m./sq.mm.	Compression Strength, Lbs./sq.in.
Samples Cored from Anodes in a Reduction Plant	1.56	58.8	6,400
	1.52	54.7	5,900
	1.55	107.0*	**
	1.55	54.2	**
	1.52	54.5	6,800
	1.54	53.0	7,100
Average	1.54	55.0	6,550
Paste Made in Plant, Baked in Laboratory	1.55	54.4	6,400
	1.52	53.0	7,100
	1.55	54.8	6,200
Average	1.54	54.1	6,600
Paste Made and Baked in Laboratory	1.54	54.6	6,900
	1.54	54.6	6,900
Average	1.54	54.6	6,900

* This high resistivity value indicates that the area sampled in the continuous anode had not completed baking. It was not included in the average.

** These samples were used for other tests and could not be crushed.

Equations for Predicting Properties of Resulting Anode Specimens from the Analysis of the Pitch.

Equations were established by Research personnel which permit the prediction of carbon properties made with the standard mixing and baking conditions. These equations and the methods used for the determination of the six properties of pitch are given in Table III.

The experimentally determined values for apparent density, electrical resistivity and crushing strength for the specimens used to obtain the equations are compared with the values predicted with the equations in Figures 5, 6 and 7, respectively.

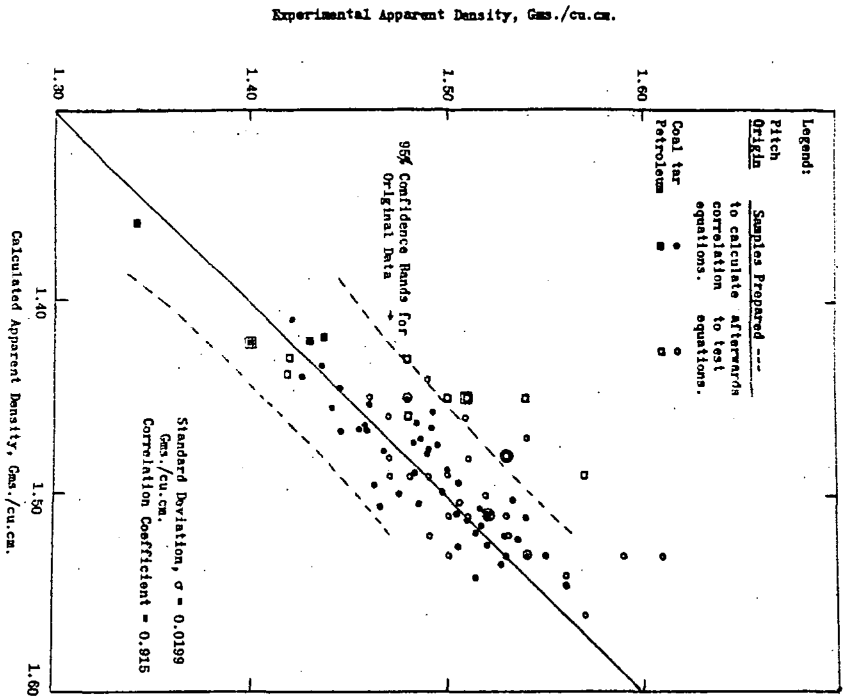

FIGURE 5. THE CORRELATION OF APPARENT DENSITY WITH VALUES CALCULATED USING THE MULTIPLE CORRELATION EQUATION.

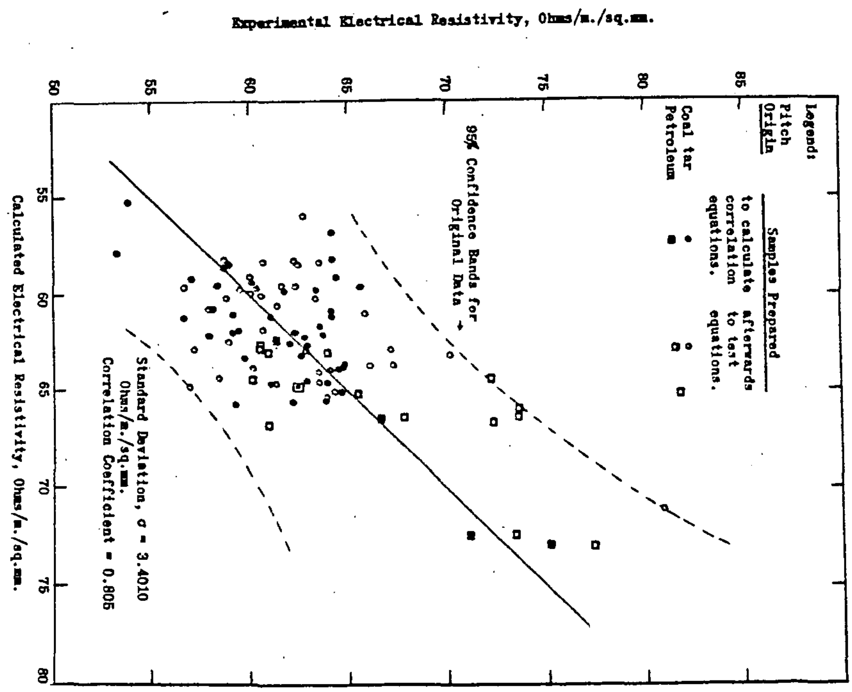

FIGURE 6. THE CORRELATION OF ELECTRICAL RESISTIVITY WITH VALUES CALCULATED USING THE MULTIPLE CORRELATION EQUATION

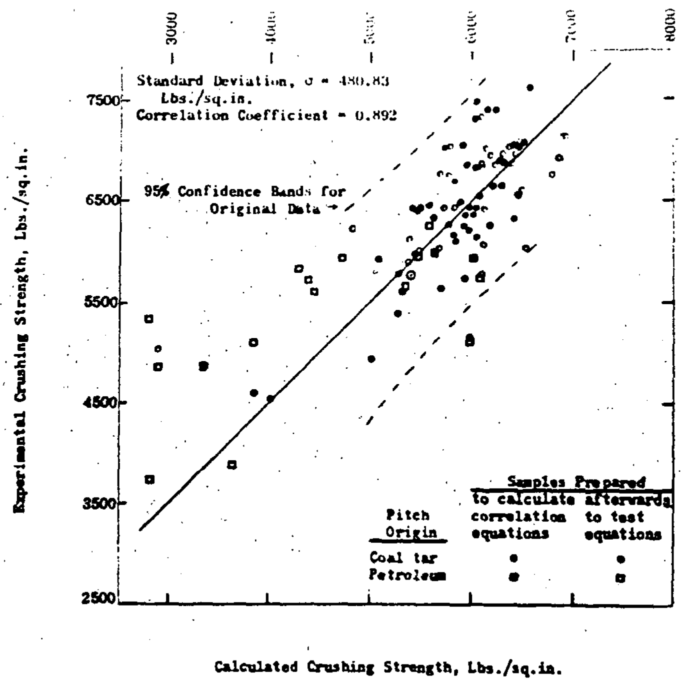

FIGURE 7. THE CORRELATION OF CRUSHING STRENGTH WITH VALUES CALCULATED USING THE MULTIPLE CORRELATION EQUATION.

The standard deviations for these measurements of apparent density, electrical resistivity and crushing strength of the specimens made with the standard conditions and commercial and experimental petroleum, oil, gas, asphalt, and regular and low-temperature coal tar pitches were 0.0199 gms./cu.cm., 3.4 ohms./m./sq.mm. and 480.8 lbs./sq.in., respectively. Correlation coefficients of 0.915, 0.805, and 0.892 were found between the predicted and experimental values for apparent density, electrical resistivity, and crushing strength, respectively. These correlation coefficients would have been 1.0 if these equations had been able to account for all the variations in the quality of the carbon.

These equations were applied to 51 additional pitches of all types. These predicted values are plotted against the experimentally determined properties on the same Figures 5, 6 and 7 to test the validity of the equations. In general, the predictions for all types of pitches were within the precision of the test methods for measuring the carbon at the 95% confidence level. The 95% confidence bands drawn on these figures were calculated only for the original 51 pitches used to develop the equations.

These equations are claimed to apply only to the type of coke, aggregate formulation, mixing and baking conditions used in this study. However, there are reasons to believe that they may be adjusted for other cokes and conditions by changing the last constant term of the equations to balance the influence of these factors on carbon properties.

TABLE II.

THE PERCENTAGE INFLUENCE OF MEASURED PITCH PROPERTIES ON VARIATIONS IN PROPERTIES OF BAKED CARBON WITH A CONSTANT AGGREGATE, MIXING AND BAKING CONDITIONS

Pitch Property	Apparent Density	Electrical Resistivity	Compression Strength
Softening Point, °C	21.43	2.98	8.28
Benzene Insoluble, %	0.59	0.39	0.16
Quinoline Insoluble, %	1.17	4.73	0.72
Coking Value, % Conradson	5.44	1.56	1.11
Specific Gravity, gms./cu.cm.	22.93	19.89	68.62
Distillation, % by wgt.			
270°C	7.45	9.78	0.56
271-300°C	5.44	4.41	0.08
301-360°C	6.44	7.06	0.0
361-400°C	6.36	6.80	0.0
Total	6.36	7.19	0.0
Total Percent of Variation Accounted For	83.7	64.8	79.6

Conclusions

Techniques for testing binder pitches provide very good comparisons between the properties of laboratory anode specimens and plant anodes.

Generally the apparent density and crushing strength of anodes increase, and the electrical resistivity decreases, as the softening point, coking value, benzene and quinoline insoluble components, and specific gravity of the pitch binder increase.

Based on the multiple correlation coefficients, it was found that 83.7% of the variations in apparent density, 64.8% of the variations in electrical resistivity, and 79.6% of the variations in compressive strength of laboratory prepared and baked carbon are accounted for in the properties of softening point, coking value, benzene and quinoline insoluble components, specific gravity and distillation through 400°C.

In general, the equations presented permit predicting the apparent density, electrical resistivity, and crushing strength of laboratory anode specimens from analyses of all type pitches within the precision of the test methods for measuring the properties of the carbon.

These equations may serve as guides for laboratories without facilities for making and testing carbon anodes. They can be used by people with limited experience in appraising pitches.

TABLE III.

EQUATIONS FOR PREDICTING RESULTING PROPERTIES OF SPECIMENS OF SODERBERG COMPOSITION FROM THE CHEMICAL ANALYSIS OF THE PITCH

APPARENT DENSITY (gms./cu.cm.)

$$= 0.00127a + 0.00048b + 0.00121c - 0.00167d + 0.60303e - 0.16131f - 0.15269g - 0.16023h - 0.16144i + 0.15997j + 0.6684$$

ELECTRICAL RESISTIVITY (ohms/m./sq.mm.)

$$= - 0.0538a - 0.0607b + 0.3906c - 0.1309d - 77.3591e + 11.1588f + 6.8737g + 9.2822h + 9.1307i - 9.2760j + 173.277$$

CRUSHING STRENGTH (lbs./sq.in.)

$$= 8.69a - 3.93b + 14.05c - 10.75d + 17{,}404e - 229.06f + 85.46g - 4.61h + 36.47i - 9.47j - 16{,}956.95$$

a = softening point, °C, cube-in-air, Barrett's method D-7.
b = benzene insoluble, %, Barrett's method B-7.
c = quinoline insoluble, % Barrett's method B-21.
d = coking value, %, Conradson, 3 g. sample, A.S.T.M. D-189-46.
e = specific gravity, g./cu.cm., 25°C, Barrett's method D-4.
f = distillation fraction 0-270°C, Barrett's method C-9.
g = distillation fraction 271-300°C.
h = distillation fraction 301-360°C.
i = distillation fraction 361-400°C.
j = Total distillate, 0-400°C.

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