

Characterization of Prebaked Anode Carbon

By Mechanical and Thermal Properties

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Laboratory tests have shown that there is a significant effect of coke source, binder content, forming method, and baking temperature on the properties of prebaked carbon. Density, mechanical strength, Young's modulus, and thermal conductivity increase and electric resistivity and anode consumption decrease as the binder content increases to optimum. Vibrated test electrodes are more sensitive to changes in coke source and binder content than pressed electrodes. The use of high amounts of anode butts has a slightly adverse effect on electric resistivity, rate of oxidation, and anode consumption, while it improves mechanical strength. Increasing the quinoline insoluble content of the pitch binder results in a higher binder requirement, improved mechanical properties, but not significantly different anode consumption. Rates of change in the binder requirement equal to 0.12 wt % per 0.01 g/cm³ increase in coke bulk density were found. Examination of plant vibrated and pressed anodes produced from the same mix showed lower density, mechanical strength, and Young's modulus for the vibrated anodes which also performed better in the potrooms.

Introduction

Raw materials used for prebaked anode production at various Alcan plant locations significantly differ in physical and chemical properties. In particular, substantial variations have been found in such properties as the bulk density of the calcined coke and the quinoline insoluble of the coal-tar pitch binder. On the process side, demands for prebaked anodes are affected by the increased demand on the world markets for aluminum, hence more cells are being put into operation and higher amperages are used. This has led to changes in baking and to the recycling of different percentages of anode butts. With regard to forming of anodes, our newer plants are using lower capital cost forming equipment, i.e., vibrators, compared to the higher cost press used before. In the midst of all these changes, there is always the question: "have anode properties been affected by raw material and process changes?" The present work was undertaken to give some insight into what effect each of these changes would have on the properties of prebaked anodes.

Test Electrode StudiesMaterials and Procedures

The results of analysis of the cokes used are given in Table I and the results of analysis of the pitch binders used are shown in Table II. The aggregates were prepared by crushing and sieving the coke into five fractions with anode butts making up the coarse fraction. The size distribution used is given in Table III.

Mixing was done in replicate at 160 to 165°C in a 10.5 litre capacity sigma-blade mixer for 40 minutes. Moulding was performed by vibration (frequency 2400 rpm; amplitude 6 to 8 mm) and pressing with a hydraulic press at the desired unit pressure, usually 40 kg/cm². Baking was carried out in a nitrogen atmosphere at 15 to 20°C/h to a final temperature of 1100°C, except in those tests where baking temperature was a variable.

The experiment to determine the effect of coke source on the test anode properties was designed as a factorial with coke source, binder content, and forming method as the factors.

Bending strength and Young's modulus were determined in a four point loading test. The laboratory anode con-

sumption test has been described previously⁽¹⁾ and most other tests are sufficiently well known to make detail unnecessary.

Results and Discussion

1. Effect of coke source, binder content, and forming method

The mean property values are listed in Table IV. A statistical evaluation showed that coke source, binder content and forming methods significantly affected the results of most properties and that significant interactions were present. The effect of coke source, binder content, and the different forming methods on density, resistivity, bending strength, compressive strength, and Young's modulus are shown in Figures 1 to 6. Empirical relationships were established in most instances. It can also be seen from the results that under the conditions chosen, the vibrated anodes are more sensitive to changes in binder and coke source than pressed anodes. In previous work⁽²⁾ it has been shown also that coke source, binder content, and forming pressure significantly affected the anode density, electric resistivity, air permeability, mechanical strength, and anode consumption. Data from the period shows that consumption decreases at the rate of 0.4% per 0.01 g/cm³ increase in coke bulk density (Collier method), 1.5% per 1% increase in binder, and 2.7% per 100 kg/cm² increase in forming pressure.

2. Change in percentage butts

The binder requirement test developed by Alcan is the amount of binder required to produce 0.02 g/cm² of packing coke adhering to the baked anode surface. The estimated binder requirement decreased at the rate of 0.12 % for each 0.01 g/cm³ increase in the Collier density of the filler coke. Hence, we must keep in mind that wide variations in the bulk density of the calcined cokes can mean large variation in production control. Similarly we have found that increases in the quinoline insolubles in the pitch have necessitated an increase in binder requirement. This has resulted in improved mechanical strength and Young's modulus but not significantly different baked anode consumption as shown in Table V.

3. Effect of baking temperature

Pressed and vibrated test electrodes made with 15.5

and 17 wt % binder and baked at 900, 1000, and 1100°C, did not show any significant change in baked density with increasing baking temperature but showed a significant decrease in electric resistivity. Bending and compressive strengths went through a maximum at 1000°C. Young's modulus followed this trend for the vibrated electrodes but the pressed electrodes made with 15.5% binder showed a decrease with increasing baking temperature. The pressed electrodes made with 17% binder had nearly the same Young's modulus for baking temperatures of 900 and 1000°C but had a sharp decrease on baking to 1100°C. In previous work⁽²⁾ it was shown that there was a significant decrease in baked anode consumption of 3% per 100°C increase in baking temperature over the baking temperature range of 1100 to 1250°C.

As the baked anode consists of butts, calcined petroleum coke and pitch coke whose thermal and mechanical properties are different it can be realized just how difficult an operation it is to produce a satisfactory prebaked anode. Obvious compromises have to be achieved to give an anode acceptable to the reduction process from both operational and economic aspects. What we have done in the laboratory is to emphasize areas of concern in the raw materials and in the production of the anode.

From these findings, we can make a good estimate of the relative differences in the property values of pressed and vibrated anodes produced from different cokes to give what we would consider the best anode. When possible, we would choose a high bulk density coke to achieve the best possible results in service. Particular advantages from this are that we would have a lower binder requirement, significantly lower electrolytic consumption, and a lower thermal gradient through the anode due to a higher thermal conductivity (15 to 20%), hence a reduction in thermal stress.

Properties of Production Anodes

Table VI shows typical properties of prebaked carbons determined on core or slab samples of anode blocks.

From the results obtained on production anodes during this work, the following observations can be made:

Effect of Processing Variables on Anode Properties

1. Aggregate size distribution and binder content

Generally, a coarser aggregate and higher binder

content give superior physical and thermal properties. It should be emphasized that for each type of coke and aggregate size distribution there is an optimum binder level. For binder contents above this value, properties deteriorate and anode performance is adversely affected.

2. Coke source

The effect of coke source is very pronounced on mechanical properties. Strength of the blocks increases with increasing coke bulk density. Even at optimum binder level, cokes of lower bulk density give lower compressive and tensile (bending) strength.

3. Butt and other anode recycle

Coarse anode butts and baked anode scrap can be used up to 50% in weight in prebaked anode aggregate without an adverse effect on physical properties. As would be expected, at high levels of butt addition a penalty must be paid in terms of electrolytic consumption and air oxidation. It is interesting to note that 50% butts when finely ground and added to the aggregate gave poor results.

4. Degree of compaction

Comparison of production anodes made by pressing and vibrating mixes of the same composition showed that the density, mechanical strength, and Young's modulus are lower in the vibrated anodes and the resistivity is not different from that of the pressed anodes (see Table VII). The vibrated anodes performed better in the potrooms than the pressed anodes. In the plant anodes it has been found also that the ultimate strain energy (i.e., the energy at which failure will occur) is more variable in pressed anodes than in vibrated anodes.

Typical Ranges of Selected Mechanical and Thermal Properties

1. Bending strength

This property in the range of 60 to 80 kg/cm² is considered adequate. Lower values measured were clearly associated with several other significant properties being inferior, in particular the resistance to thermal stresses.

2. The ratio of bending strength to modulus

The ratio x 10³ is within the range of 0.80 to 1.00

for most of the acceptable formulations. Values of 0.55 to 0.80 were found for mechanically inferior blocks, while figures from 1.00 to 1.15 were associated with too brittle blocks. It is interesting to note that total strain at failure may be changed by as much as 25% by changes in processing variables.

3. Thermal shock index and thermal stress resistance

These appear to be the best criteria of block quality with respect to thermal cracking. A minimum of 50 to 60 seconds is required for the former, and a value of 1.50 or higher is desirable for the latter. Thermal shock index is the time measured in seconds which is required to crack a 5 mm thick and 50 mm diameter carbon disc exposed to the flame of a gas burner under controlled conditions. Thermal stress resistance (or Gangler relation) is defined as follows:

$$R = \text{Therm. stress resis.} = \frac{\text{Bending strength} \times \text{Thermal conductivity}}{\text{Young's modulus} \times \text{Coefficient of thermal expansion}}$$

and

$$E = \text{Max. strain energy} = \frac{(\text{Bending strength})^2}{2(\text{Young's modulus})}$$

4. Thermal conductivity and thermal expansion

In order to reduce thermal stresses in an anode block high thermal conductivity and low thermal expansion values are required. Thermal conductivity varies between 3.5 and 5.5 W/m°C for most prebaked anode formulations. It is affected to a greater extent by processing variables than by raw material source. Coefficients of thermal expansion lie in the range of 3.5 to 5.0 x 10⁻⁶/°C. This property is sensitive to coke source, it increases with increasing coke bulk density.

5. Consumption by electrolysis and air oxidation

The range in baked anode consumption for blocks with acceptable physical properties is relatively small. Typical values would be between 114 and 116%. Anode consumption is given as percentage of that corresponding to formation of CO₂, i.e., 0.247 lb or 0.112 kg per kWh. Typical air oxidation rate figures for prebaked anodes are 0.080 to 0.120 g/cm² h. The effect of metallic

impurities in the coke on oxidation rate is clearly recognizable.

Conclusions

Coarser aggregates and higher binder contents give generally superior physical and thermal properties. The effect of coke source is very pronounced on mechanical properties, strength of the blocks increases with increasing calcined coke bulk density. Recycled butts and other baked anode return can be used up to 50 wt % in the aggregate without a significant adverse effect on physical properties of the blocks.

Based on plant performance of blocks at various Alcan locations, a mechanical strength (in bending) of 60 to 80 kg/cm² is considered adequate. The ratio of bending strength to Young's modulus x 10⁻³ lies between 0.80 and 1.00 for most of the acceptable formulations. The range in total strain at failure is 25% and this is attributed to changes in processing variables. It appears that a minimum thermal shock index of 60 seconds and a thermal stress resistance of 1.50 are required for blocks of acceptable quality. The effect of coke source on baked anode consumption and the effect of coke impurities in particular vanadium content on air oxidation rate were easily recognizable.

References

- Hollingshead, E.A., and Braunwarth, V.A., Laboratory Investigation of Anode Consumption in the Electrolytic Production of Aluminium. Extractive Metallurgy of Aluminium, Vol. 2, 31-50. Interscience 1963.
- Rhede, P., A Review of Factors Affecting Carbon Anode Consumption in the Electrolytic Production of Aluminium. Light Metals 1971, pp 385-406. Proceedings of Symposia 100th AIME Annual Meeting, New York 1-4 March 1971.

TABLE I
PROPERTIES OF VARIOUS CALCINED PETROLEUM
COKE USED IN LABORATORY PREBARED ANODE STUDIES

PROPERTY	Coke 1	Coke 2	Coke 3	Coke 4
Hydrogen	0.19	0.18	0.05	0.19
Carbon	97.3	97.0	98.8	97.2
Sulphur	1.68	3.02	1.67	2.35
Ash	0.32	0.74	0.73	0.53
Real density	2.03	2.03	2.01	2.03
Mean crystallite thickness, μ c	26.1	25.8	22.2	26.0
Electric resistivity $10^{-4} \Omega$ cm	475	490	485	480
Reactivity to CO ₂ cm ³ /g.s	0.10	0.077	0.071	0.089
Porosity %	26.6	32.2	30.4	29.4
Bulk density (20 x 35 mesh) g/cm ³	0.881	0.822	0.789	0.852
Hardgrove grindability index	40.0	37.0	41.0	39.0
Surface area 200 x 325 mesh m ² /g	0.50	1.00	0.50	0.75
Iron %	2.80	3.40	2.90	3.10
Silicon %	0.029	0.033	0.051	0.031
Vanadium %	0.026	0.024	0.041	0.025
Nickel %	0.011	0.022	0.009	0.016
Other %	0.009	0.007	0.008	0.008
Titanium %	0.030	0.001	0.070	0.015

*Coke 4 is a 1:1 mixture by weight of Cokes 1 and 2.

TABLE V
EFFECT OF PITCH SOURCE ON TEST ELECTRODE PROPERTIES

SOURCE	Coal Tar			Petroleum
	OI = 14.5 %	OI = 18.1 %	OI = 1.0 %	
Binder content	15.6	16.2	14.0	
Green apparent density	1.582	1.591	1.560	
Baked apparent density	1.497	1.511	1.465	
Apparent binder coke yield	68.6	69.6	56.7	
Vol. change on baking	+1.3	0	-0.80	
Calculated porosity	27.1	26.6	25.5	
Air permeability	6.4	7.2	20.5	
Electrical resistivity	71	69	85	
Compressive strength	252	393	180	
Bending strength	62.3	78.5	36.5	
Young's modulus (bending) 10 ³ kg/cm ²	70.6	94.6	61.0	
BS/YM ratio x 10 ⁻³	0.88	0.85	0.60	
Total strain x 10 ⁻³	1.06	1.01	0.85	
Thermal shock	(time) s	35.6	34.1	
Air oxidation rate	g/cm ² h	0.103	0.109	
Anode consumption	%	115.0	116.4	
			116.5	

TABLE IV (continued)

COKE SOURCE	COKE 3		COKE 4	
	0.789	0.852	29.4	0.852
Coke bulk density, g/cm ³	14.9	15.5	17.0	18.5
Binder Wt %	1.36	1.363	1.397	1.476
Green app. density, g/cm ³	1.519	1.514	1.547	1.569
Baked app. density, g/cm ³	1.479	1.436	1.459	1.471
Binder coke yield, wt %	69.7	71.2	72.2	67.4
Volume change on baking %	-0.66	-0.87	-1.46	-1.03
Porosity %	35.4	34.6	32.8	30.3
Air permeability, cm ² /sec	27.0	28.8	27.9	27.1
Resistivity, 10 ⁻⁴ ohm cm	21.9	23.5	26.0	13.25
Bending strength, (BS) kg/cm ²	107	95	78	67
Young's modulus (YM) 10 ³ kg/cm ²	15.6	19.8	27.8	51.5
BS:YM x 10 ⁻³	23.1	27.2	32.5	58.7
Total strain at failure x 10 ⁻³	0.66	0.73	1.01	0.88
Compressive strength, kg/cm ²	86	134	199	306
Thermal conductivity, W/m°C	2.56	2.74	2.97	3.98
Coef. of thermal exp., 10 ⁻⁶ /°C	3.28	3.43	3.57	3.63
Thermal shock, seconds	4.53	3.23	3.07	2.80
Thermal stress resistance, (R) x 10 ³ kg/cm ²	27.3	25.7	25.9	30.4
Max. strain energy, (E) x 10 ⁻³ kg/cm ²	5.40	7.21	11.89	22.79
*V and P denote vibrated and pressed electrodes respectively.	18.32	25.28	30.45	41.05
**Coke 4 is a 1:1 mixture by weight of Cokes 1 and 2.				

TABLE VI

TYPICAL PROPERTIES OF PRODUCTION ANODES
DETERMINED ON SLAB OR CORE SAMPLES

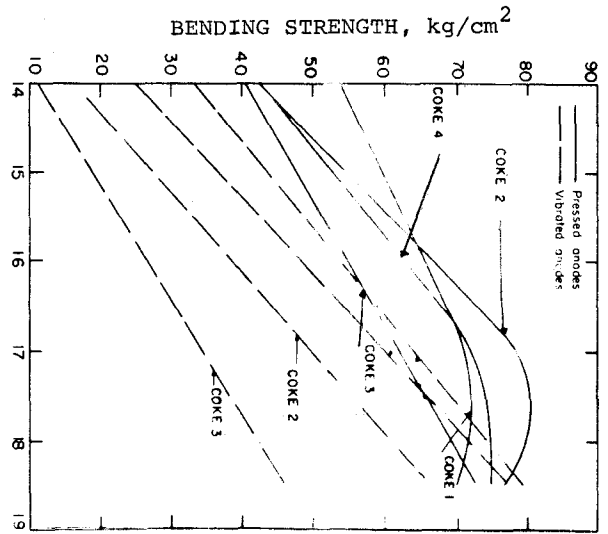
TYPE OF COKE USED		HIGH BULK DENSITY	LOW BULK DENSITY
Butt content in aggregate	wt %	25	25
Optimum binder content	wt %	14.5	16.0
Green apparent density	g/cm ³	1.608	1.570
Baked apparent density	g/cm ³	1.554	1.530
Air permeability	cm ² /sec	10.0	60.0
Resistivity	10 ⁻⁴ ohm.cm	46.0	56.0
Bending strength (BS)	kg/cm ²	80.0	69.0
Young's modulus (YM)	10 ³ kg/cm ²	70.5	68.0
BS:YM x 10 ⁻³		1.14	1.01
Strain at failure x 10 ⁻³		1.20	1.06
Compressive strength	kg/cm ²	480	310
Thermal conductivity	W/m°C	5.60	5.30
Coeff. thermal expansion	10 ⁻⁶ /°C	3.75	3.50
Anode consumption	%	114.5	117.5
Air oxidation rate	g/cm ² .h	0.200*	0.120
Thermal shock index	sec	50 to 70	50
Thermal stress resistance	R x 10 ³	1.66	1.54

*High-vanadium coke.

COMPARISON OF PROPERTIES OF PRESSED AND
VIBRATED PRODUCTION ANODES

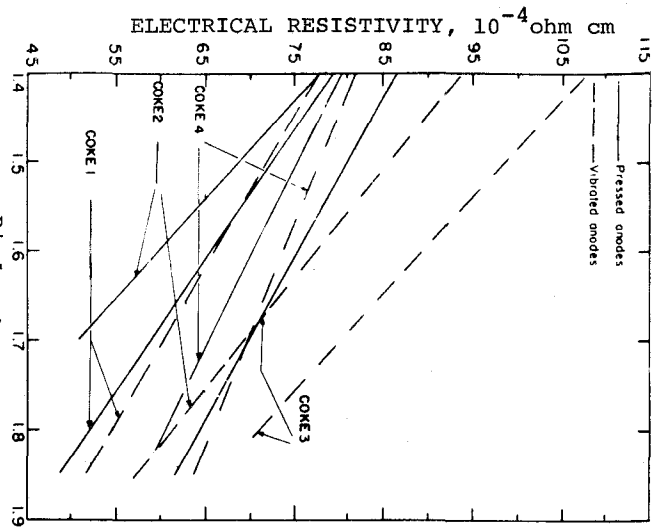
TABLE VII

PROPERTY	FORMING METHOD (at identical binder content)	
	Pressing	Vibration
Baked apparent density	1.520	1.490
Electric resistivity	59	57
Compressive strength	365	325
Bending strength	72	67
Young's modulus	84	77



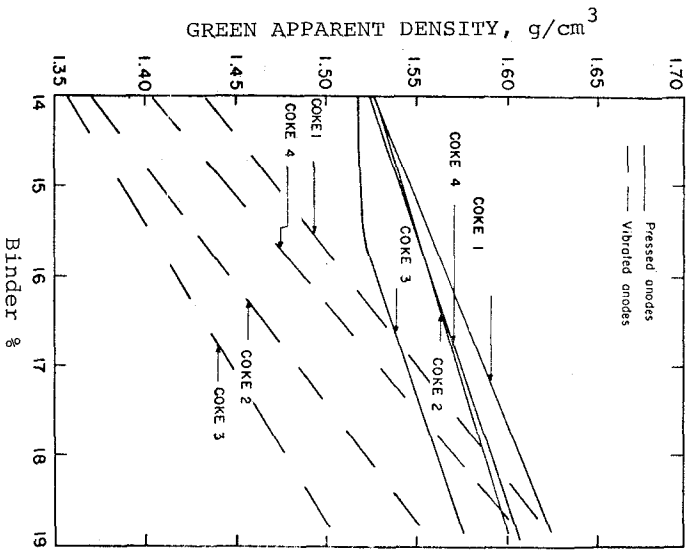
BENDING STRENGTH AS A FUNCTION OF BINDER CONTENT, COLLIER BULK DENSITY OF FILLER COKE, AND FORMING METHOD.

FIGURE 4



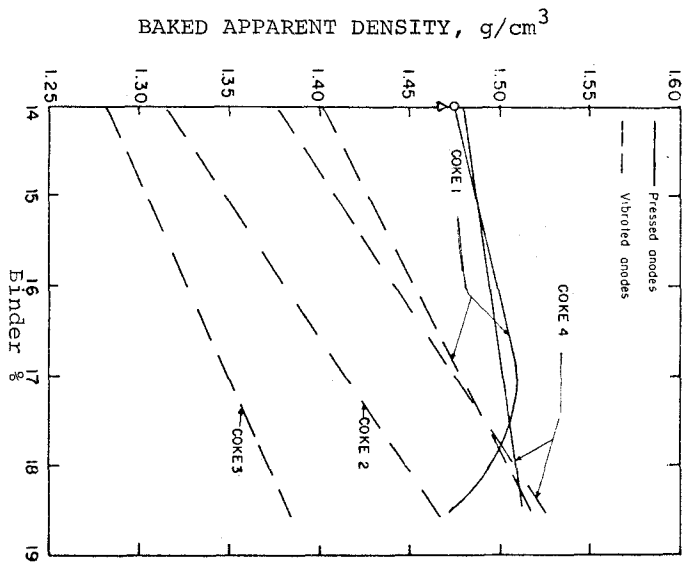
ELECTRICAL RESISTIVITY AS A FUNCTION OF BINDER CONTENT, COLLIER BULK DENSITY OF FILLER COKE, AND FORMING METHOD.

FIGURE 3



GREEN APPARENT DENSITY AS A FUNCTION OF BINDER CONTENT, COLLIER BULK DENSITY OF FILLER COKE, AND FORMING METHOD.

FIGURE 1



BAKED APPARENT DENSITY AS A FUNCTION OF BINDER CONTENT, COLLIER BULK DENSITY OF FILLER COKE, AND FORMING METHOD.

FIGURE 2

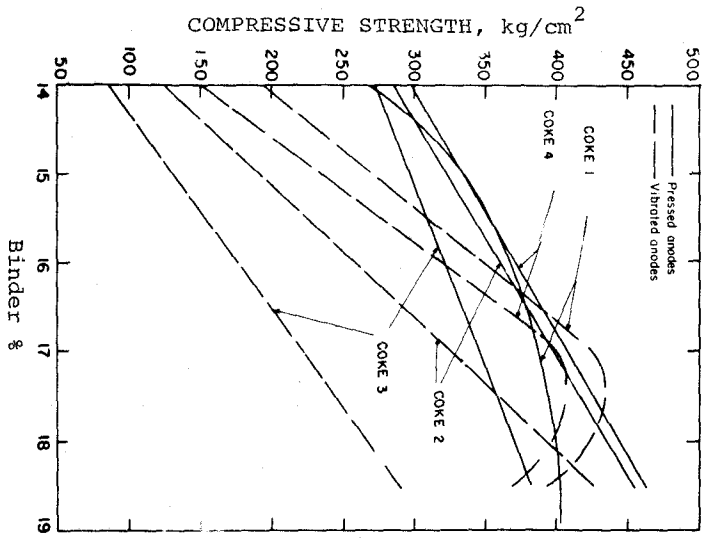


FIGURE 5
 COMPRESSIVE STRENGTH AS A FUNCTION OF
 BINDER CONTENT, COLLIER BULK DENSITY
 OF FILLER COKE, AND FORMING METHOD.

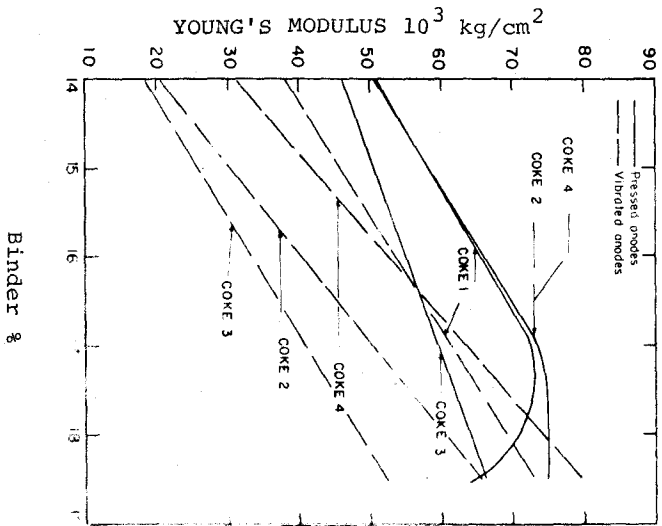


FIGURE 6
 YOUNG'S MODULUS AS A FUNCTION OF
 BINDER CONTENT, COLLIER BULK DENSITY
 OF FILLER COKE, AND FORMING METHOD.