PROCESS FOR THE PRODUCTION OF PETROLEUM TAR PITCH FOR ANODE MANUFACTURING.

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INTRODUCTION

The aluminium production involves the consumption of petroleum coke and pitch, which are used in the manufacturing of anodes. Normally carbon consumption, as anode, lies between 0.4 and 0.48 Kg of carbon per Kg of metal produced[1]. In the same manner, the amount of pitch used in preparing the anode lies between 14 and 18 mass %, and varies with the chemical composition of the pitch, the porosity and the structure of the petroleum coke.

The estimated amount of pitch required to meet the world aluminium production, for the early 90's, will be in the range of 1.2 million tonnes per year[2]. Additionally, almost all binders used in the manufacturing of electrodes are derived from high-temperature coal treatment during the production of metallurgical coke. However the Enviromental Protection Agency (EPA) regulations on the benzene emissions from coking oven equipment, have lead to recent announcements of numerous coking oven closures in the United States[2]. According to PACE Consultants[2], metallurgical coke output in the US is expected to plummet to 17 million short tonnes by 1996 from 25 million short tonnes in 1990.

Coke battery closures in the US, resulting from the EPA mandates, should reduce the supply of good quality coal tar pitch in the US by as much as 25 to 30 %[2]. One can assume that a similar trend should be observed in other major areas of coal tar pitch production.

Naturally, it is highly desirable to provide a continous closed-process for the producction of high quality tar pitch suitable for electrode manufacturing. In this sense, INTEVEP the R&D Center of Petroleos de Venezuela, has carried out a research project to develop a process scheme for the production of a high quality petroleum pitch for use as a binder in anode manufacturing, using Fluid Catalytic Cracking Decanted Oil as feedstock. This paper presents results of this research as well as properties of the petroleum pitches obtained.

EXPERIMENTAL RESULTS

Feedstock selection and characterization: The main characteristic of coal tar pitch is that it is a highly condensed material with an aromatic content higher than 90 volume %. With this in mind, FCC decanted oil, a highly aromatic refinery stream, was selected as the feedstock. Table 1 presents the properties of this material.

Process Description: The process for the production of petroleum tar pitch was developed using Intevep's pilot plant facilities. The process route and product yields are shown in the fig.1 and table 2, respectively. The fresh feed, decanted oil, is fed to the filter so as to remove undesirable solids, mainly FCC catalyst particles, the clean filtered stream is thereafter fed to a preheater-coil heater where the temperature is increased to 430 °C. The heated feedstock is treated in a soaker type reactor, where sufficient residence time is provided for polymerization and condensation reactions to take place. Four different residence times were considered (TR1: 39 min, TR2: 78 min, TR3: 117 min, and TR4: 156 min). The stream leaving the soaker is sent to a high pressure separator, where C_4 minus hydrocarbons and light distillates are taken off from the top, and a heavier fraction is withdrawn from the bottom. The heavier fraction is finally sent to a reduced pressure pipe still so as to produce a gasoil and a petroleum pitch. By carefull selection of pressure and temperature in this final stage a high quality petroleum tar pitch can be produced.

Pilot Plant yields and product characterization: Table 2 presents typical yields and product qualities obtained when the decanted oil is processed at a temperature of 430 °C and a pressure of 15.6 bar-a. Carbon value (CCR), density and softening point meassurements showed that residence times TR1 and TR2 were not sufficient to yield a highly condensed petroleum pitch.

Petroleum pitch selection and preparation: From table 3, pitch TR3 has properties similar to those of a typical coal tar pitch used for anode manufacturing, on the other hand, pitch TR4 has higher softening point and viscosity values than those found for coal tar pitch. Nevertheless, its higher carbon content ought to yield a denser anode. In order to improve on these properties and still benefit from the high severity conditions at which this pitch was obtained, pitch TR4 was mixed with another aromatic and lighter petroleum fraction known as light cycle oil. The resultant mixture, TR4D contained 7 volume % of light cycle oil.

Finally, bearing in mind the importance of quinoline insolubles, as a coal tar pitch quality guideline, a fourth pitch TR4DNH was prepared by adding 7 mass % of carbon black to the TR4D pitch.

Evaluation of Intevep Petroleum Pitches: Four samples of petroleum pitch (TR3, TR4, TR4D and TR4DNH) were sent to a specialized laboratory in Switzerland, for analysis as a binder material for the production of carbon anodes for the aluminium industry. The work involved the determination of physical and chemical properties of each pitch as well as production and testing of a series of bench scale test anodes according to this particular laboratory's standard procedure. Physical and chemical properties of the pitches evaluated are presented in Table 3., together with corresponding values of a typical commercially available petroleum pitch and standard coal tar pitches used in the aluminium industry. For each pitch a series of 20 cylinders (50 mm in diameter) were produced at four separate pitch levels, these are 14, 16, 18 and 20 mass %. For each series mechanical properties, reactivity in CO_2 and air, and chemical analysis were performed.

DISCUSSION:

PITCHES

General: The main differences observed between coal tar and petroleum pitches are as follows:

- At comparable viscosity levels the softening point of the petroleum pitch is about 5 to 10 °C higher. This is due to the different temperature-viscosity interdependence of the two products.
- Petroleum pitches contain hardly no quinoline insolubles (QI). The QI present in coal tar pitches are due to the carry over from the coke oven during the carbonization process of mineral coal.
- The amount of QI in coal tar pitch reflects the severity of the pyrolisis and therefore, the pitch aromaticity, so that the aluminium industry specifies QI levels very closely. However, for petroleum pitches the aromaticity is independent of the QI content thus it is not relevant to consider this property in its specifications.
- Density in water of petroleum pitches is about 5-10 % lower than that for coal tar pitches (this being due to the different nature of the organic compounds) but is not detrimental as long as the coking value lies in an acceptable and comparable range to that of coal tar pitch. Furthermore, it is important to point out that previous work found in the literature has shown that anodes produced from petroleum pitches are inferior in baked density, strength and air permeability to those produced from traditional coal tar pitches. However, petroleum pitches have been successfully used as a binder in the aluminium industry where they have been specifically developed for a particular end user[3]

Softening point: TR4 pitch was found to be extremely hard and viscous, with a softening point that would make it unpractical for mixing in the paste plant.

TR3, TR4D and TR4DNH showed softenig points that are more usual. The viscosities also fall withing the typical values found for thermally cracked petroleum pitches.

Insolubles in toluene: Toluene insolubles is the most significant property for distinguishing between a thermally cracked and oxidized petroleum pitch. Values below 10 mass % for TR3, TR4, TR4D and the commercially available pet-pitch, illustrate the fact that they were produced by a thermal process. The higher value observed for the TR4DNH pitch is a result of the addition of about 7 mass % of carbon black, as artificial QI.

Insolubles in quinoline: This fraction is almost zero, as would be expected for a thermally cracked petroleum pitch. The TR4DNH sample has been blended with 7 mass % of carbon black, therby allowing for the effect of artificial addition of QI to be quantified.

Coking value: The coking value was higher than typically expected for all four petroleum pitches under consideration. This is advantageous in anode production since the greater the amount of residual coke, the higher the anode baked density (assuming all others parameters remain constant).

Distillation: The distillation of the TR4D and TR4DNH samples is their biggest drawback, as far as pitch properties are concerned, especially in the 0-270 °C range. The amount of these *volatiles* as *well* as their *carcinogenic* nature would pose significant problems in the paste plant. In the case of TR4D, this amount (6.57 mass %) in the 0-270 °C range is a direct result of the addition of a light cycle oil during the pitch preparation.

For TR3 and TR4, fractions obtained during distillation are much lower and can be considered more typical.

Density in water: TR3 pitch shows a value which is within the typical range for thermally cracked petroleum pitches, whereas the other three samples show lower but acceptable values for this property.

Elemental analysis: The elemental impurities of the four pitches are typical and would be acceptable to the aluminium industry.

BENCH SCALE ANODES AND PROPERTIES

Figures 2, 3, and 4 present the results of the evaluation of the bench scale anodes prepared with each of the INTEVEP petroleum pitches. Following is a discussion of the most relevant aspects of this evaluation:

TR3 Pitch (Fig. 2):

The optimum pitch content is around 14% this being 2% absolute less than for a typical coal tar pitch. This fact is of great financial consideration as the price of pitch is usually twice that of the coke. At this optimum the physical properties of anodes are within the range of those obtained with coal tar pitches. Although the compressive strength is at the lower end of the range this will not be too serious a problem if proper mixing, forming and baking conditions are chosen in an industrial scale plant.

As the permeability level (4.8 nPm at 14% pitch) is almost typical (3-4 nPm) for bench scale anodes and as the reactivities in CO_2 and air are quite normal, this pitch will give anodes having an acceptable burning behaviour in the pots.

TR4 (Fig. 3)

The poor wettability of this pitch, evident from the low green and baked apparent densities and the compressive strength, is a direct consequence of the high softening point and subsequent poor mixing during green paste manufacture. This effect becomes particularly evident at 20% pitch addition where the baking loss and shrinkage differ markedly form the trend observed at the lower pitching levels. The CO_2 reactivity is, despite the poor physical properties, better than typical and reflects the good quality of the baked pitch coke resulting from its higher anisotropy.

TR-4D (Fig. 4)

The physical properties of anodes made from this pitch are within the range of those measured for typical coal tar pitch based anodes, the only significant exceptions being air permeability, which is about twice the value typically expected and compressive strength which is at the lower end of the range. Although poor air permeability will result in a higher carbon consumption during electrolysis, this is offset to some degree by the lower CO_2 reactivity losses of the binder-matrix.

TR-4DNH

The addition of 7 mass % carbon black has severly affected the physical properties of the test anodes due principally to a blinding effect that has hindered the wettability of the pitch.

CONCLUSIONS

Intevep TR3

Of the four Intevep pitches tested this was found to be the most siutable as the majority of properties were within typical coal tar ranges. Although the compressive strength of the anodes were at the lower end of the range, a paste plant optimization would improve this behaviour. A significant "selling point" for this pitch is the lower optimum content needed in anode manufacture.

Intevep TR4

The TR4 pitch was unsuitable due to its high softening point resulting in inadequate fluidity and subsequently poor mixing.

Intevep TR-4DNH

The addition of 7 mass % carbon black to TR-4DNH was found to have a detrimental effect on the test anode properties.

Intevep TR-4D

The results indicate that the TR-4D pitch is promising although further investigations would be needed into production techniques that could improve its distillation behaviour, mechanical strength and air permeability.

REFERENCES

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2. The pace consultants Inc. Petroleum Coke Markets Potential. November 1990.
3. R&D Carbon Ltd. Evaluation Program for Intevep Petroleum Pitches. April 90.

TABLE 1. FCC DECANTED OIL CHARACTERIZATION

SPECIFIC GRAVITY	1.078
API	-0.2
SULFUR % WT	2.6
CCR % WT	6.3
SOLIDS, PPM	15
ASH, PPM	41
FLASH POINT, °C	68
KINEMATIC VISCOSITY, cst	
KV @ 38°C	476
KV @ 60°C	118
AROMATICS, % WT	79
DISTILLATION D-1160	
% VOL	TEMP. °C
5	318
30	408
50	436
80	517

TABLE 2. TYPICAL YIELDS AND PRODUCT QUALITY

YIELDS		
	GASES	9.3
	LIGHT DISTILLATES	21.1
	GASOIL	40.8
	PITCH	28.8
LIGHT DISTILLATES CHARACTERIZATION		
	SPECIFIC GRAVITY	0.8610
	SULFUR, % WT	1.36
	DISTILLATION:	
	IBP	114
	10	167
	30	231
	50	280
	90	370
	FBP	372
GASOIL CHARACTERIZATION		
	SULFUR, %WT	3.8
	SPECIFIC GRAVITY	1.1014
	VISCOSITIES, cst	
	KV @ 60°C	28.5
	KV @ 100°C	5.9
	FLASH POINT, °C	207.7
	DISTILLATION	
	IBP	261
	10	334
	30	366
	50	390
	90	442
	FBP	490

TABLE 3. PITCH PROPERTIES

PROPERTIES	UNIT	COAL TAR PITCH TYP. RANGE	COMM PET. PITCH	TR-3	TR-4	TR-4D	TR-4DNH
SOFTENING POINT METTLER.	°C	100-110	121.7	129.8	148.5	114.5	121.8
VISCOSITY BY 140 °C	cP	3000-6000	n.m	n.m	n.m	10'250	12'720
VISCOSITY BY 160 °C	cP	600-1500	2140	4280	n.m	1952	2590
VISCOSITY BY 180 °C	cP	150-300	406	696	4820	458	676
DISTILLATION 0-270°C	%	0.1-0.6	0.1	1.4	0.5	6.5	6.8
DISTILLATION 0-360°C	%	4-8	8.4	9.8	8.4	17.5	15.0
DENSITY IN WATER	Kg/dm^3	1.30-1.32	1.244	1.240	1.257	1.148	1.151
COKING VALUE	%	54-60	52.8	55.7	58.3	57.2	61.4
WATER CONTENT	%	0-0.2	<0.1	<0.1	<0.1	<0.1	<0.1
INSOLUBLE IN QUINOLINE	%	8-14	0.5	1.0	0.4	0.65	7.9
INSOLUBLE IN TOLUENE	%	28-36	8.5	8.9	8.2	10.0	17.5
ASH CONTENT	%	0.1-0.3					
ELEMENTS							
S	%	0.3-0.5	3.01	2.52	2.77	2.48	2.41
Na	ppm	100-400	110	98	82	70	97
Ca	ppm	20-80	21	25	23	17	38
Cl	ppm	100-300	41	34	30	30	37
Al	ppm	50-200	96	285	232	237	227
Si	ppm	50-200	74	271	276	284	398
Fe	ppm	50-300	63	199	146	166	191
Zn	ppm	100-600	15	17	4	5	5

FIGURE 1. INTEVEP PILOT PLANT PROCESS ROUTE FOR THE PRODUCTION OF PETROLEUM TAR PITCH

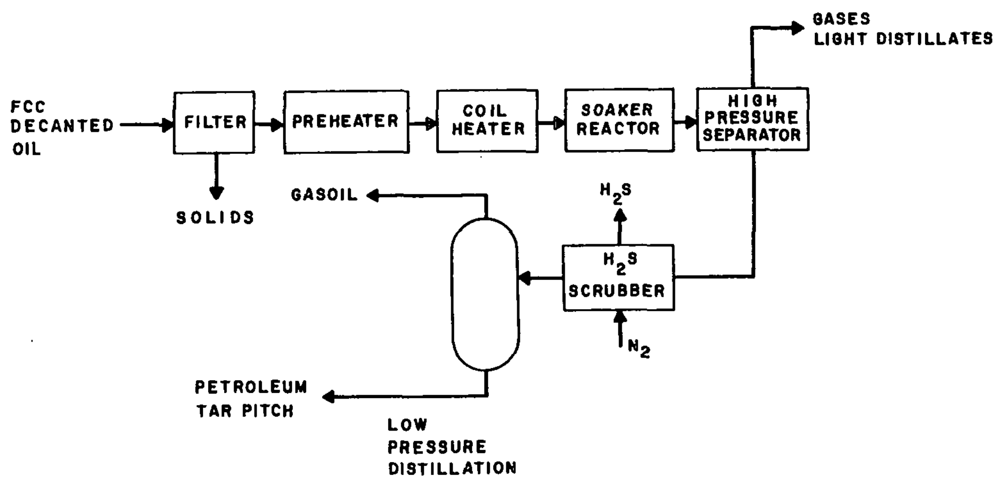

FIGURE 2. BENCH SCALE ANODE EVALUATION USING PITCH TR3

PITCH CONTENT: A = 14% B = 16% C = 18% D = 20%

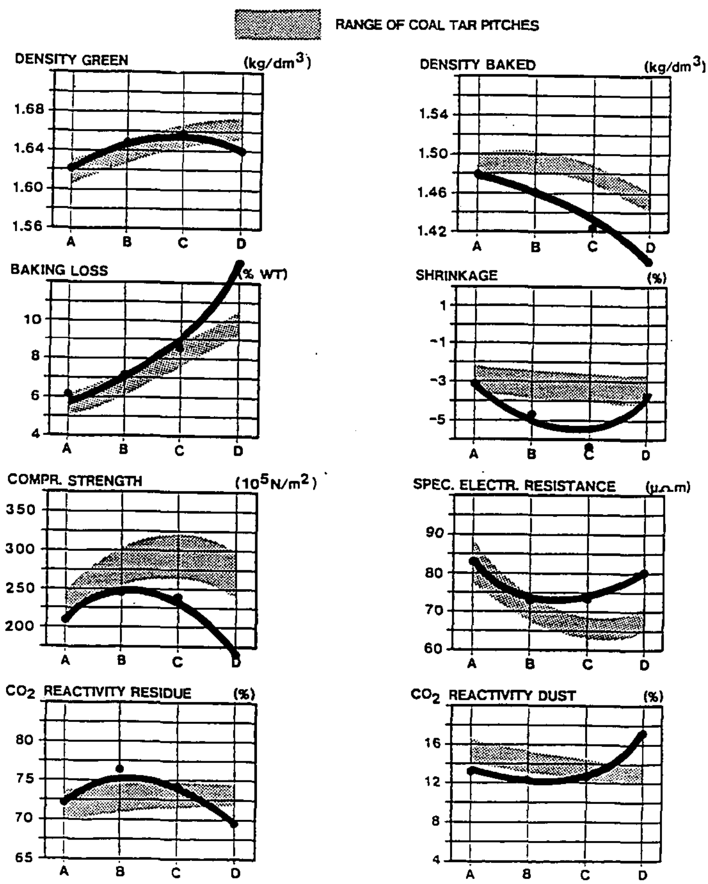

FIGURE 3. BENCH SCALE ANODE EVALUATION USING PITCH TR4

PITCH CONTENT: A = 14% B = 16% C = 18% D = 20%

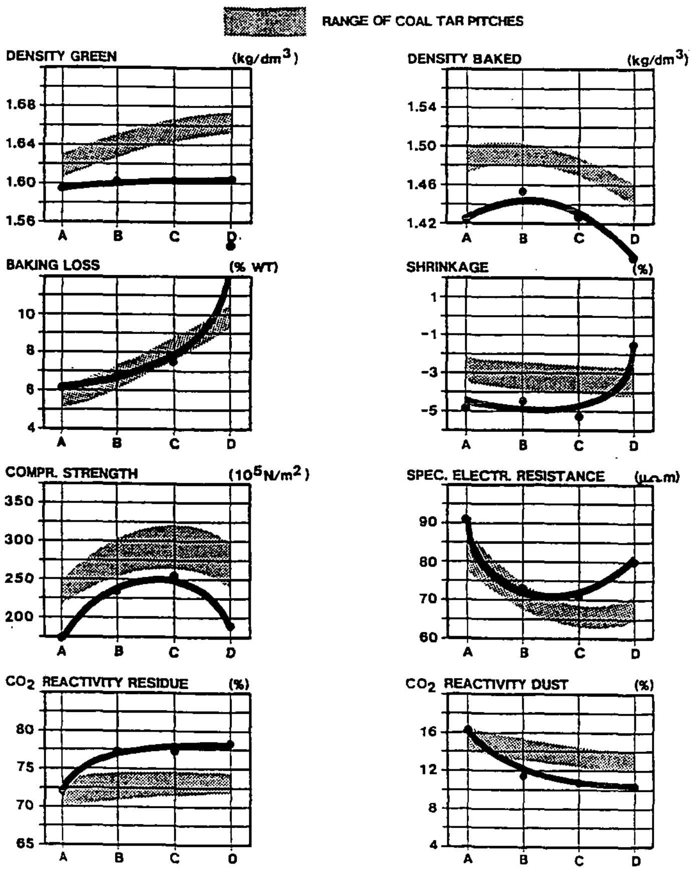

FIGURE 4. BENCH SCALE ANODE EVALUATION USING PITCH TR4D

PITCH CONTENT: A = 14% B = 16% C = 18% D = 20%