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BINDING CHARACTERISTICS OF COAL TAR PITCHES FOR PREBAKED ANODE MIX - CHOICE CRITERIA

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The properties normally required of pitches to be employed in the manufacture of prebaked anodes are high specific gravity and high intrinsic yield of carbon.

Certain pitches, however, meet these criteria but are nevertheless found not to be entirely satisfactory in actual industrial use. In contrast, pitches which fail to satisfy the same criteria can in certain cases be employed to obtain the desired physical characteristics in the plant or in the laboratory.

This being so, Aluminium Pechiney now relies more especially on laboratory testing to determine the ability of a pitch to soak into a mass of coke. We believe the coke yield of the pitch can be improved by enhanced penetration at the green anode stage.

The analyses carried out reveal new criteria governing pitch selection and provide an explanation of the importance of the nature of the alpha-resins and of pitch viscosity at the mixing temperature.

1 - Introduction

The criteria governing the choice of pitches by aluminium producers were originally arrived at on the assumption that intensively cracked heavy tars would be available in sufficient quantity.

More recently, periods of tight supply as compared with demand for tars prompted both producers(1,2) and users to consider employing pitches deriving from tars which were, on the face of it, less suitable and, as it happens, the characteristics of the anodes obtained proved to be satisfactory.

The authors have, for instance, investigated in the laboratory two pitches deriving from very different types of tar. The materials investigated had undergone only moderate thermal cracking and had very different properties (densities 1.29 and 1.32 g/cc, respectively, and SERS fixed carbon contents of 47.5 and 52.2 % respectively). Despite this, the physical characteristics of agglomerates produced in the laboratory were found to be satisfactory and virtually identical.

The results of the laboratory investigation were subsequently fully borne out by a trial under actual industrial conditions, when successful use was made of a pitch deriving from a light tar, the ability of which to "wet" the coke entirely compensated for its intrinsically low carbon yield.

The selection criteria to be applied (3) therefore had to be revised in order to encompass a broader range of tars. New methods of analysis have also had to be employed.

This paper discusses the methods developed in Aluminium Pechiney's analytical laboratory and/or pilot plant to determine pitch characteristics, with particular reference to ability to wet and soak into a body of coke grains.

Although the results reported refer only to coal tar pitches, the majority of the methods discussed are of course applicable to petroleum pitches.

2 - Assessment of pitch in terms of binding performance

A pitch will only perform well as a binder if it is easily able to occupy - i.e. "wet" -the whole of the available surface area of the separate grains of solid which have to be cemented together.

The notion of wetting introduces the property of surface tension. However, as will emerge from the discussion of the porosity to liquid pitch of a body of coke, viscosity is also a contributing factor.

In most cases, it is possible to show that a temperature exists above which a pitch will, under certain conditions, spread spontaneously over a bed of coke. This temperature is measured by the "spreading drop test".

The influence of the quinoline-insoluble alpha-resins on pitch quality is such as to warrant special attention, comprising the determination of the C/H ratio of these resins and examination under the microscope. The electronic microscope has been used to reveal the special rôle played by the mesophase in the pitch-and-coke mixing process.

The laboratory investigation was supplemented by the production in the pilot plant of pressed agglomerates (diameter 90 mm) in order to determine, inter alia, the impact of pitch characteristics on the densification under pressure, and on release from the mould, of a pitch/coke mixture.

2.1 - Surface tension

The surface tension of a pitch is estimated by determining the force required to just balance that acting on a strip of platinum immersed in the liquid pitch. The force so determined is proportional to the surface tension.

The characteristics of the substance under test - high viscosity and the changes induced by heating - are such that the determination of surface tension is anything but simple, as evidenced inter alia by the work done in this connection by GREENHALGH and MOYSE(4). The procedure employed by the authors included :

- working under a stream of nitrogen,
- first coating the platinum strip with a thin film of pitch, thus reducing the contact angle to nil,
- carrying out the determination at temperatures ranging from 170 to 250° C for a pitch with a METTLER softening point of 100° C.
  The viscosity of the pitch at these temperatures ensured acceptable measurement times.

Figure I shows some experimental results for four coal tar pitches. The corresponding analytical data are set out in Table I. Pitch B was prepared in the laboratory by heating Pitch A in the oven in a sealed container and without mixing for 30 days at 200° C to determine the effects of ageing.

It will be seen that :

(i) The effects of heating are only slight as regards surface tension, which shows a small reduction, but are substantial as regards softening point, fixed carbon, beta-resins, viscosity and drop spreading temperature. The value of surface tension would, therefore, seem to be more closely related to the parent tar than to the heat treatment undergone by the pitch.

(ii) Surface tension does not vary systematically in step with any other characteristic of the pitch (beta-resins, viscosity or drop spreading temperature). It therefore constitutes a specific item of information which has to be taken into account, together with the results of the more usual types of tests.

2.2 - Porosity of a body of coke to liquid pitch

Maximum densification of a pitch/coke mix would require the total penetration by the pitch of the inter- and intra-granular porosity exhibited by the coke grains.

The degree of penetration can (cf. Figure II) be determined by reference to :

- residual pore volume (not including sealed pore volume),
- the pycnometric density of the coke,
- the equivalent pore diameter to which penetration is effective.

The extent to which penetration is effective will depend on the pycnometric fluid and the pressure employed.

A CARLO ERBA 70 mercury porosimeter was modified for use with hot pitch as the pycnometric fluid. Since the determination of change in volume was based on the maintenance of electrical contact by means of the mercury, the latter had to be conserved as the intermediate medium. The final design of the pycnometer is illustrated by Figure III).

Results obtained under various experimental conditions are shown in Table II.

The pitch viscosity was adjusted by simply varying the temperature of a soft pitch, measuring times being short enough for it to be reasonably assumed that no chemical changes occurred.

It will be seen that a sufficient reduction in viscosity ensures a degree of penetration which is as complete as obtained with mercury under pressure and, in fact, a pycnometric density equivalent to that obtainable with helium as the pycnometric fluid (ca. 2.025 g/cc).

The conclusion is that viscosity has a fundamental impact on pitch penetration under industrial conditions, where pitch/coke contact time will inevitably be, at best, of the order of those employed in the laboratory investigation reported.

2.3 - Spreading drop test

The ability of a pitch to wet a coke can be defined by reference to the angle of contact made by a drop of pitch deposited on a plane coke surface. A zero angle means complete wetting. The practical measurement of the contact angle is, however, complicated by the roughness of the coke surface. The ability of a pitch to wet a coke can be clearly determined by means of the "spreading drop test", based on work done by AUBERT (5).

Pitch	A	B	C	D	E	F	G	H
Melting point METTLER °C	106	132	107	90	114	104	93	109
Fixed carbon SERS %	52.5	56.1	58.5	50.4	55.2	54.2	45.2	55.3
Density g/cm^3	1.314	1.316	1.346	1.308	1.314	1.312	1.284	1.322
α resins %	10.7	10.4	19.6	10	12.5	10.6	3.7	11.8
β resins %	20.6	27.4	16.7	17.7	21.9	21.4	12.3	21.7
$\alpha+\beta$ resins %	31.3	37.8	36.3	27.7	34.4	32	16	33.5
C/H	1.74	1.82	1.92	1.73	1.73	1.72	1.60	1.77
$(C/H)_\alpha$	3.47	3.27	3.97	3.55	3.1	3.72	2.99	3.26
Viscosity at 160 °C mPa.S	860	17000	1800	240	3100	1400	240	1700
Surface tension at 160 °C mN/m	40.6	39.6	37.1	27.4	28.5	34	30	27
Spreading drop test °C	155	191	>250	130	213	158	127	158

TABLE I : Analytical data

Fluid	mercury	mercury	pitch	pitch	pitch
Pressure, bars	1	400	1	1	1
Viscosity, mPa.S			1000	100	10
Pycnometric density of coke g/cm^3	1.695	2.023	1.91	1.965	2.025
Residual open porosity mm^3/g	96	0.3	28	5	≈ 0
Equivalent diameter of pores reached, µm	15	.01	.5	.25	≈ 0

TABLE II : Porosimetric data

10^{-6} m	A	E''	E
1 - 10	30000	18500	21000
10 - 20	2300	1350	1300
20 - 30	500	400	700
30 - 40		40	100
40 - 50			120
50 - 60		30	30
60 - 70			
70 - 80			
80 - 90			5

TABLE III : Mesophase (units/mm^3)

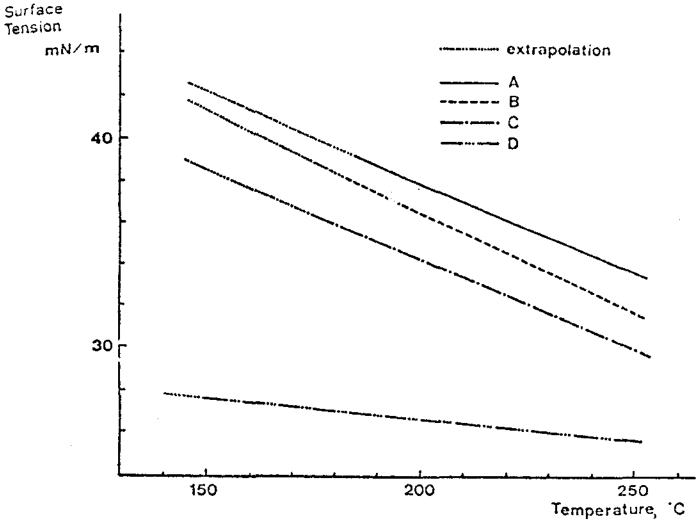

FIGURE I

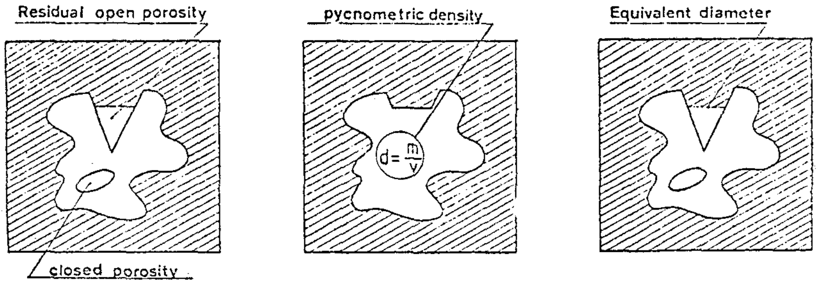

FIGURE II : Porosimetric analysis

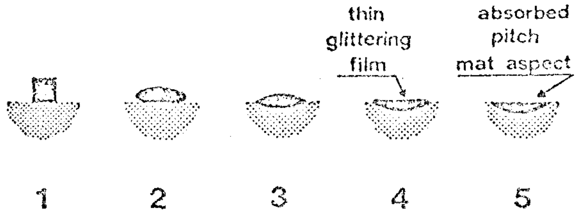

FIGURE IV : Spreading drop test

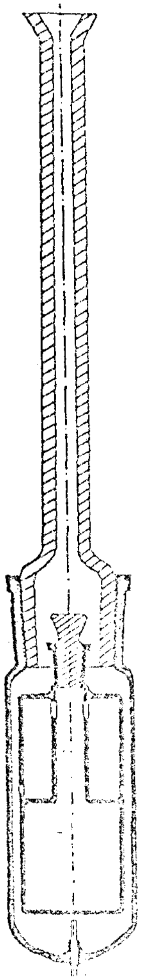

FIGURE III : Liquid pitch pycnometer

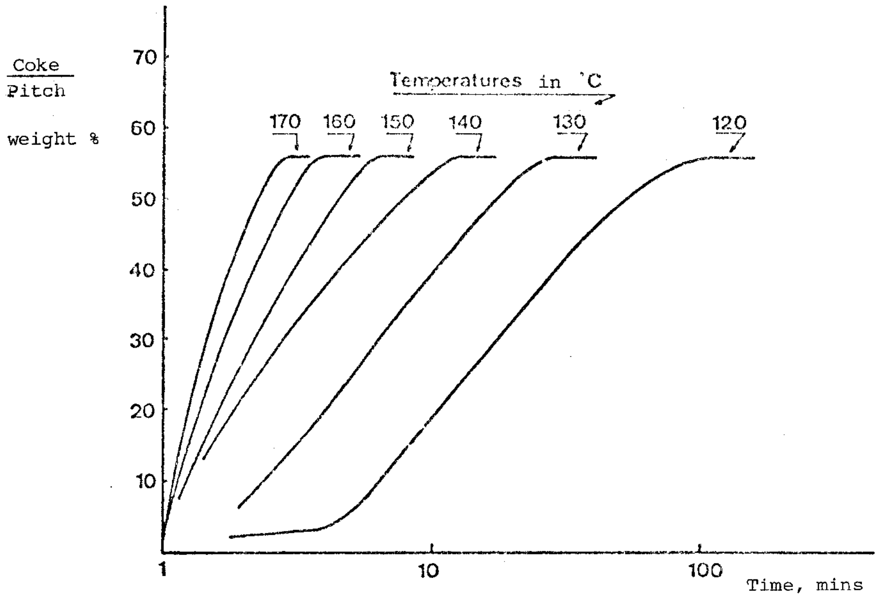

FIGURE V : Spreading drop test

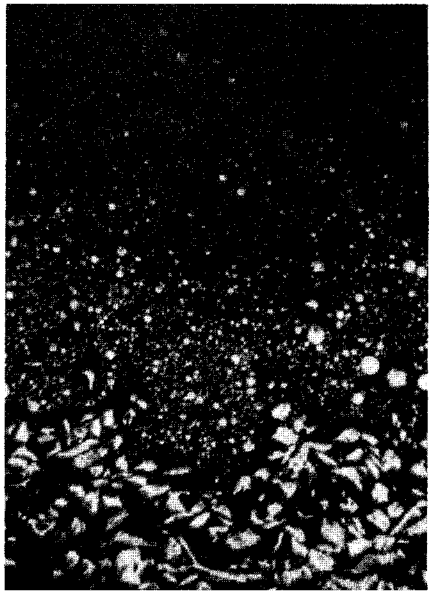

FIGURE VI : Cross-section of a drop deposited on coke grains (pitch E)

A moulded pellet of pitch (diameter 6 mm, height 4 mm) is deposited on a bed of coke of particle size 48/100 Tyler mesh (0.235/0.147 mm). The whole is then heated under nitrogen at the rate of 3° C per minute and the temperature T_d noted at which the pitch is completely absorbed by the bed of coke (Condition 5, Figure IV).

Generally speaking, Condition 5 is separated from Condition 4 by no more than a few degrees Centigrade. Where this is so, and provided the pitches in question originate from the same class of tar, there will be a correlation between the value of T_d and other characteristics of the pitch (softening point, alpha- and beta-resins content).

The phenomenon under consideration would appear to be one of viscous flow through the bed of coke, which acts as a sieving medium. The factors affecting the flow are :

(i) the pitch/coke contact angle,

(ii) the viscosity of pitch, given that the experimental results are substantially affected by the temperature gradient selected.

Figure V also shows that variations in the weight of coke agglomerate with the weight of pitch are unaffected by temperature over a wide interval.

As against this, the time required for agglomeration (i.e. for the pitch to flow into the pore spaces) increases sharply as the temperature is reduced.

(iii) the relative sizes of the various "solid" particles contained in the pitch (carbon blacks and mesophase) and the bed of coke considered.

Figure VI illustrates the gradual "sifting" of the mesophase by the coke and of the remainder of the pitch by the mesophase.

Table I, showing analytical data for various pitches, provides a measure of the sensitivity of the spreading drop test.

Pitches can be divided into three categories, viz :

(a) those with outstandingly high wetting power (D and G) and which are completely absorbed by the bed of coke at 35 - 40°C above their METTLER softening points,

(b) those with more average wetting power (A, F and H) and which are absorbed at 45 - 55°C above their softening points,

(c) those with poor wetting power (C and E). Pitch E is the subject of the photomicrograph shown in Figure VI. Pitch C performs similarly by virtue of its high content of alpha-resins.

2.4 - Determination of alpha-resin C/H ratio

The nature of the alpha-resins is known(6) to have a significant effect on pitch properties. One aspect of this has just been mentioned and it will further be seen (§ 2.6) that these resins can also be of special importance to the pitch/coke wetting process.

The two tests most commonly carried out with respect to alpha-resins are their quantitative determination and the determination of the $(C/H)_{\alpha}$ ratio, i.e. the ratio of the number of carbon atoms to the number of hydrogen atoms in the alpha-resins.

The C/H ratio is directly dependent on the relative quantities of carbon blacks $(C/H > 4)$ and of mesophase $(C/H \approx 2)$.

The C/H ratio, however, offers no more than a rough guide, as can be seen from Figure VII, which records the results of periodic analysis of commercial supplies of seven families of cokes over a period of approximately six months. Families 1 to 5 inclusive are European pitches; families 4 and 5 come from the same coke plant and are representative of two production runs; families 6 and 7 are American pitches.

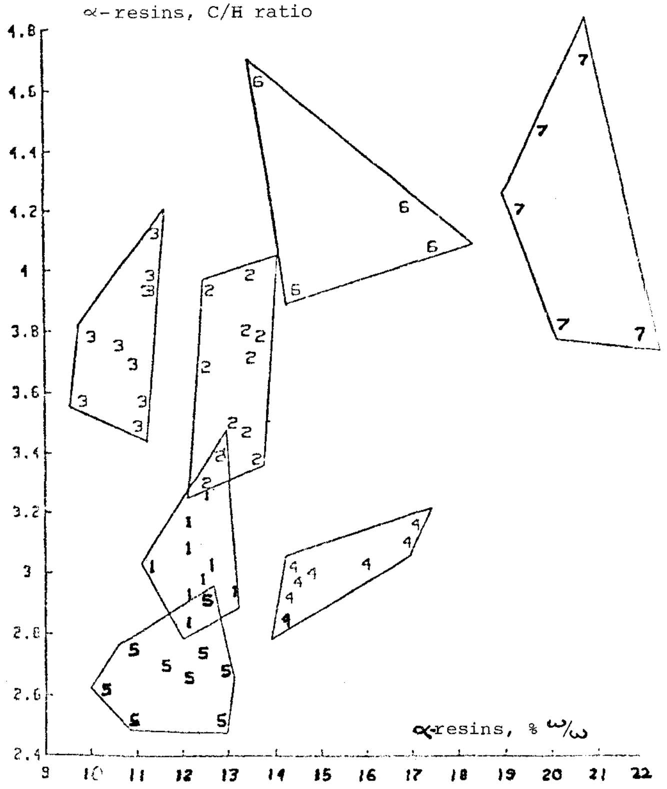

Figure VII

2.5 - Examination under the optical microscope

This is the only way of determining the true quantity of mesophase and also its particle size distribution.

The photomicrographs in Figure VIII refer to two types of pitch which differ significantly in terms of mesophase content (Pitches F and E).

The optical microscope can be employed to carry out a size count, as shown in Table III. The analytical data for pitches A and E are given in Table I. Pitch E^{**} is of the same family as pitch E. Pitches A and E^{**} were found to perform normally on the spreading drop test (with rapid progress from condition 4 to condition 5). Pitch E was found to perform as illustrated by Figure VI.

The size of one micron was estimated from the resolution of the optical microscope employed. However, a large number of mesophase "seeds" are probably of size below the limit of optical resolution and, therefore, not detectable by this procedure.

2.6 - Examination under the electron microscope

2.61 - Carbon blacks

Fine examination of this fraction of the alpha-resins requires a magnification in excess of that obtainable with the optical microscope.

Examination under the electron microscope showed pitches to contain every species of carbon black - in isolation (Figure IXa) or associated in chain form (Figure IXb) or as flakes (Figures IXc and IXd).

The size histograms constructed(7) point to a two-part distribution pattern, one being centred between 2000 and 3000 Å and the other at below 1000 Å. A high proportion of carbon blacks of large size would appear to be a desirable feature.

2.62 - Mesophase

Figure X shows the appearance of the carbon mesophase of a pitch and how it attracts carbon blacks to its surface as it grows.

The lines observed on the spheres of mesophase are deformations caused by cutting with the ultramicrotome. The very considerable fragility which this suggests is confirmed by other investigations(7) and is to be explained by the structure of the mesophase.

The mesophase is so fragile that it is completely disorganised by even the mildest forms of mechanical action. More to the point, the mixing process as normally practiced destroys the greater part of the spheres initially observable in the pitch.

At the same time, the coke grains become coated with the broken-up constituents of the mesophase (Figure XI).

The resultant disorganisation of the mesophase is, however, too great to be reversible on baking, so that the baked carbon originating from the mesophase is microporous, reactive and only weakly adherent to the coke originating from the other pitch fractions.

This being so, the existence of any substantial proportion of mesophase at the mixing stage will adversely affect the mechanical strength and reactivity of the baked anode.

2.7 - Investigation of laboratory agglomerates

The technique employed in the investigation of 90 mm dia. agglomerates has been discussed in earlier publications(8,9), and was originally developed in connection with research into anode forming conditions (pressure and temperature) using particular raw materials.

Similarly, using a set of standard conditions enables various pitch and coke combinations to be investigated and this approach was applied to the study of agglomerates produced from a coke of a predetermined type and particle size distribution in admixture with various pitches.

The discussion will be confined here to results obtained at the pre-baking stage, to indicate how the pitch employed modifies the *compactibility of the mix* under a particular set of experimental conditions (150°C and 450 bars pressure).

Figure XIIa illustrates variations in the apparent densities of the agglomerates after release from the mould for three coal tar pitches (F, G and H). The relevant analytical data is shown in Table I.

Any differences in apparent density on release from the mould are seen to be small, at ca. 0.01 g/cc, despite the very considerable differences in the pitches as expressed by the analytical data.

Figure XIIb shows variations in agglomerate volume under pressure, expressed as litres per 100 kg of coke.

There are seen to be fairly pronounced differences in terms of the compactness of the mix under pressure. The maximum densification of dry solids obtainable with pitch H was found to be almost 3 % lower than with pitch G.

As a result, pitch G, although of distinctly lower density, *enables* agglomerates to be obtained which are of higher apparent density than *achievable* with pitch H.

The point of saturation with pitch, above which volume under pressure increases, and the physical significance of which has already been discussed(8), is .7 % higher for pitch G than for pitch H.

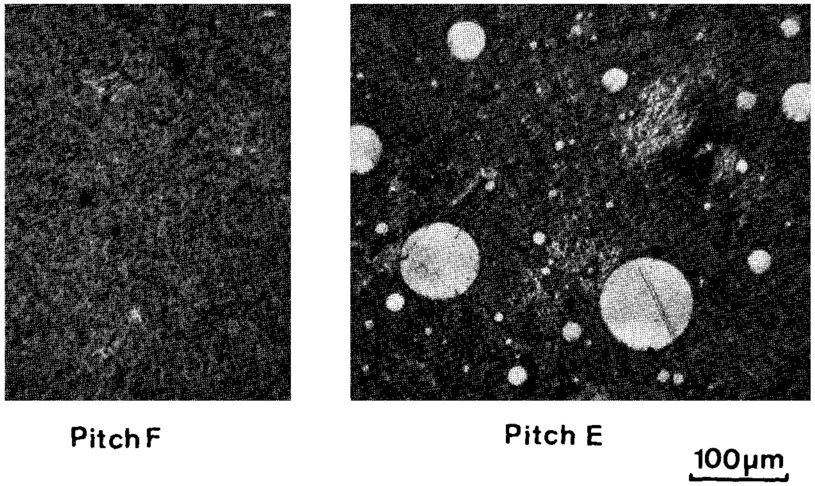

FIGURE VIII

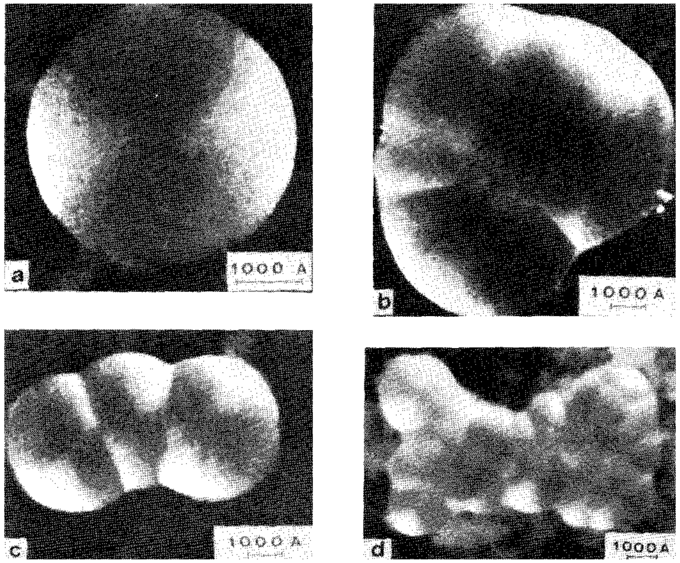

FIGURE IX : Examination of carbon blacks under the electron microscope

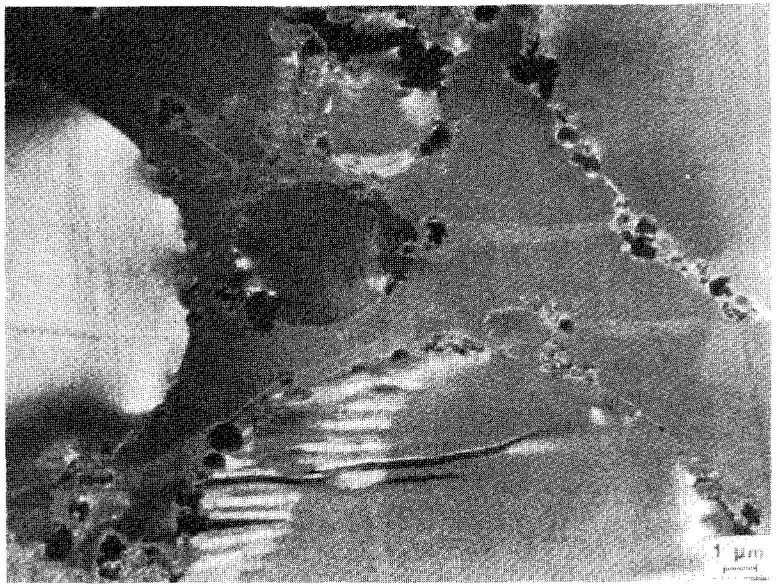

FIGURE X : Examination of pitch E under the electron microscope

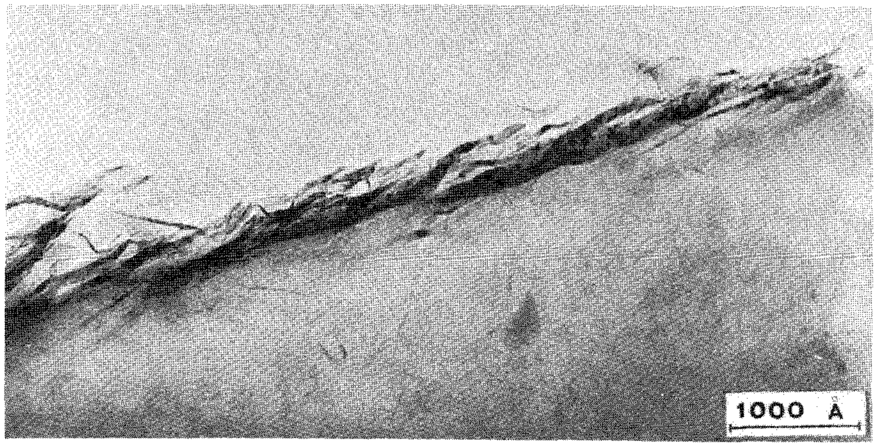

FIGURE XI : Fine coke grain coated with coke ex-mesophase

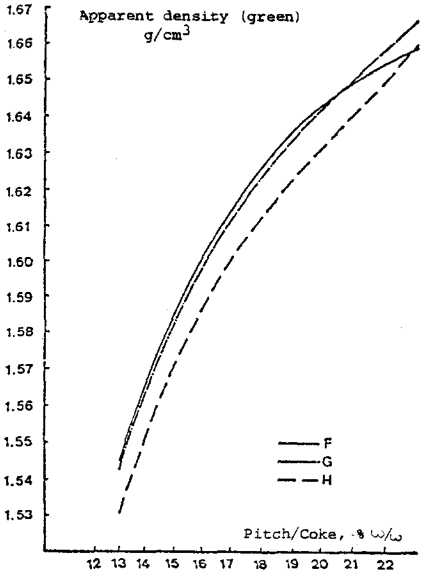

FIGURE XII a

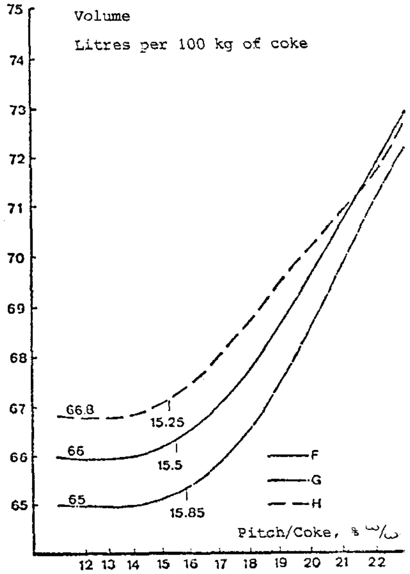

FIGURE XII b

3 - Conclusions

The specified requirements of high density and high intrinsic yield of carbon are appropriate only to tars which are rich in solid carbon particles by virtue of intensive cracking in the coke oven.

Lighter tars cannot be expected to meet these requirements. They can, however, be entirely suitable for use if their ability to wet a body of coke is developed by the right sort of heat treatment.

Increased penetration of the coke by the pitch and greater compactibility of the bed of coke produce a denser anode paste and improve the coke yield of the pitch.

The need is to determine, for each tar, the optimum heat treatment enabling the lightest fractions to be removed :

- without leading to the formation of any substantial quantity of *mesophase at an advanced stage (diameter of 10 microns or more)*,
- and with minimal increase in viscosity.

These objectives would, on the face of it, appear to rule out the specification of a softening point which takes no account of the nature of the parent tar. They should also mean a levelling off, or even a fall, in average softening points, which have increased steadily over the last decade.

Pitch selection will henceforth be guided by laboratory methods enabling coke wetting power to be determined, combined with examination under the microscope and the production of experimental 90 mm dia. agglomerates.

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