

WORLDWIDE PITCH QUALITY FOR PREBAKED ANODES

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ABSTRACT

A worldwide survey made on pitches supplied to Al smelters provides valuable information with regards to the typical values and specifications for binders.

The document reviews the effect of coke oven parameters on tar characteristics as well as distillation features on pitch properties. It provides an overview of the ISO analytical standards used for characterizing pitch, and includes guidelines on the specification settings. The link between pitch characteristics and anode performance is also summarized.

Addressing the evolution in the coke oven and tars distillers' industry over the last decades, it further discusses future challenges for the successful production and usage of binders.

INTRODUCTION

The Al industry consumes about 2.2 million tons/year of binder pitch for the production of carbon anodes. Pitch properties are influenced not only by the nature of the tars, but also by the distillation process. Both these are adapted to the target specifications of the end user.

Today, there are as many specifications as the number of carbon plants, and therefore, delivering pitch to the customers' satisfaction still remains a challenge.

The large variety of specification properties and methods as well as the scatter of their levels are, of course, related to the peculiarities of carbon plants and the well-known conservatism of end users' requests for unchanged product characteristics regardless of the evolution and changes in the feedstocks and carbon plant equipment.

This lack of adaptability resulted, for instance, in the crisis of 'mesophase' rich pitch which shows poor wetting performance. It is also the reason for the usage of intrinsically inferior quality low softening pitch, regardless of improvements in the mixing / forming / cooling technologies. The worldwide knowledge obtained from the different tars and the performance of anodes in smelters allows for the appropriate selection of raw material property targets. It also prompts for sound adaptation of the preheating, mixing and forming steps in the carbon plants

During an independently conducted research, Ph.D. thesis Hulse [1] contacted 75 different prebaked anode plants to establish the typical conditions used to manufacture anodes across the western world (FSU and China are currently under examination). The findings made on pitch quality and usage aspects are revisited

here with a goal of simplifying the specifications approach for the mutual benefit of the user and producer.

PITCH PRODUCTION

Coal Tars and the Steel Industry

Coal tars used by distillers for the production of binder are a by-product of cokeries where metallurgical cokes are produced for pig iron production in blast furnaces (0.8 t of coke per t of pig iron). Pig iron, together with some steel scraps, is poured into Basic Oxygen Furnaces (BOF) where the excess carbon is oxidized by a stream of oxygen in order to produce the desirable crude steel.

This process, though in competition with the growing Electric Arc Furnace process (40 % share) where only scraps are used (no coke reductants), is still producing around 500 million tons/y of crude steel [2]. The specific quantity of coke needed for pig iron production tends to decrease as direct pulverized coal injection gains in importance. However, there are still about 350 million tons/y of metallurgical coke produced from about 450 million tons/y of coal.

On the basis that coal used in cokeries contains 3.3 % tar, around 15 million tons/y of coal tar become available. Most of it, is in fact, burnt as fuel (and is generally priced against low sulfur fuel oil); as the worldwide demand of coal tar pitch is about 3 million tons/y this means that less than 7 million tons/y of tars is required to meet this demand.

Although there are still plenty of tars available globally, North America has a tar deficit in excess of 30% due to coke oven closures [3], while the largest coal tar producer in China (4 million tons/y) has more than 3 times the amount required for internal binder demand.

Unfortunately, intercontinental and inland transportation of tars is problematic and costly. The lack of locally produced tar in the US was the driving force for distillers to look for lower cost petroleum based streams to extend their binder pitch production. [4]

Coal Tar Generation and Preparation

A typical coke plant with two coke batteries, each having 100 coking cells with a production of 20 tons of coke per day, has a capacity of producing more than 1 million tons/y of coke and 35'000 tons/y of tars.

On each side of the coking cells fuel is fired to maintain wall temperatures in the range of 1050-1100 °C. The coarse grained

coal blend is transformed into a fissured lump coke bed releasing steam, ammoniac, benzol and tar vapours (25 % of the coal are volatiles). Due to the presence of oxygen in coal the native tars contain up to 10 % of phenol (C_6H_5-OH) and low naphthalene (2 benzene rings). The latter compound is formed later due to the contact of the benzene with hotter coke layers and oven walls; at the same time the phenol content decreases down to 0.1 %. [5]

In the free cavity above the charge, extensive thermal degradation takes place, in $\sim 10 - 20$ seconds, resulting in carbon black like spheres of $\sim 1 \mu m$ and also in highly anisotropic pyrolytic carbon particles of $100 \mu m$. Multi polycyclic molecules are formed at the same time.

The presence of oxygen due to air ingress into the chamber enhances cracking reactions. The severity of these may be quantified by measuring the phenol content in tars by liquid chromatography and the ratio between alkyl naphthalene/naphthalene [6], by C_{13} NMR, (decreases with higher severity). It is simpler to consider the C/H ratio and the specific gravity values of the tars that increase with severity. It has been established that high severity (temperature) tars give better coking value pitch than low severity (temperature) tars; thus, better electrode quality is often reported for high C/H or specific gravity tar and pitch.

The parameters influencing the formation of heavy (> 3000) and medium (1000 to 3000) molecular weight carbon black components are listed below. High severity tars are produced with:

- coals with high volatiles content
- high coking temperature
- low volume chambers
- high air ingress rate

With regard to the design for heating the carbonization chamber, the system developed by Koppers Company in the US and Canada favoured high severity tar cracking. In this system the flues within one heating wall are connected to the crossover flues that transport the combustion gases over the top to the flue system in the next heating wall. [7]

In Europe and the Far East there are no crossover flues and temperature/residence time above the carbonization chamber are lower, leading to lower severity tar production. This and other aspects mentioned explain the systematic difference found in tars and later in pitches produced independently of the distillation process.

During charging of the chamber, carry-over particles of coal, char and coke breeze of different sizes (25 to $500 \mu m$) entrain the gas stream leaving the coke oven [8]; these particles are rich in ash (up to 10 %) and contaminate the tar.

In older plants, charging with disconnected gas eliminated any carry-over, but, dust emission is the draw-back. A complete collection of gas and dust connected to the tar recovery increases the carry-over tar by up to 1 % and results in a substantial increase of ash well above 0.1%. Complete dedusting in a separate dust collection system is probably the best option for pitch distillers and users.

Mineral matter from the refractory is only found in tars produced in poorly maintained coke ovens. However, an enrichment of "soluble" metals, like Pb and Zn that form organometallic compounds is systematically observed. These two metals in tar and pitch are comparable to the V and Ni present in resids and petroleum coke as these are built in the feedstocks. For anode manufacturing, a blend can be made in order to control these concentrations.

The preparation of coal tar in a cokery, from vapour to the clean tar tank, is shown in figure 1. [9]

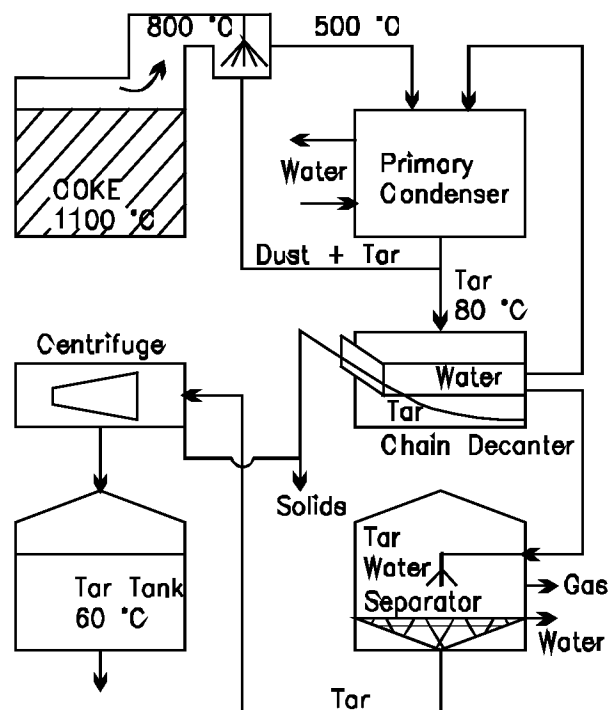


Figure 1: Tar preparation prior distillation

In the condensing section, severe quenching by means of recycled ammonia water gives off a liquid mixture that is decanted to separate some of the water and the coarser carry-over (chain scraper). A more intense separation is obtained from on-line centrifugation reducing carry-over to about 0.1 %. Carbon black material is not separated as these particles are much smaller in size.

Water reduction (typically from 5 % to 1 – 2 %) is obtained by adding surfactants in conical shaped separators, but with state of the art high centrifugation, values with less than 1% are achieved. Removal of water is important, as it contains up to 1% of corrosive chlorine in the form of ammonium salt. This is formed by the reaction of chlorine ash in the coal with ammonia gases ($3 \text{ kg NH}_3/\text{t coal}$). Today, a minimum chlorine content of 100 ppm in tar is achievable and this guarantees a minimal requirement of sodium (150 ppm) for the neutralization of the tar prior to distillation.

Tars with low water/chlorine content reduce the risk of over-neutralization from soda and this leads to anodes with better resistance against gas oxidation. [10]

Tars from the Oil Industry

Pure petroleum pitches have been manufactured for decades and were used in the Al-industry prior to the 1973 crisis.

Ashland Petroleum Company developed a proprietary commercial petroleum pitch process in the mid 60's that was introduced into the speciality graphite market where not only high purity is a pre-requisite, but also good crystalline graphite structure. Examples of feedstocks that can be used include decant oil from the fluid catalytic cracker units, product aromatic extracts of lube oil process, hard asphalt from solvent deasphalting units and pyrolysis tar from naphtha and gas oils used for the production of ethylene.

Obviously the degree of aromaticity of such tars is much lower than coal tars as the severity of cracking conditions is much lower (500 vs. 1100 °C). Even though the carbon content of the corresponding pitch is generally lower, these petroleum streams were found to be appealing for replacing depleted coal tar sources or to produce low Poly Aromatic Hydrocarbon (PAH) binders, especially for Söderberg paste applications. [11, 12]

Pitch Manufacturing

As the carbon (coking) value of the tars is too low, distillation of the light oil components is mandatory for good electrode properties

The original tar stills operated by means of a batch method. These were directly heated with flue gas to temperatures exceeding 400 °C. At first, a fractionation column and a condenser provided chemical oil followed by a creosote oil distillate. Due to frequent fires and low productivity these were systematically replaced from 1940 by continuous units. Here, the tars are heated up in tubular heaters, a pipe developed for the petroleum industry. In this unit only a small volume of turbulently flowing tar is rapidly heated without any coking activity at temperatures below 400 °C. In the 1950's all development in tar distillation aimed to optimize the volume and quality of, at that time, valuable oils like naphthalene and anthracene. [13]

During this time and until 1960, the main application from pitch was the binder used for briquette manufacturing from the coal fines, a soft pitch with a softening point of 20 °C lower than the electrode pitch that was systematically produced. Electrode pitch was produced by implementing a further heat-treatment step where soft pitch was heated, often batch-wise using HTM circuit at around 400 °C for several hours at atmospheric pressure.

With the progressive increase of the softening point, this treatment process was pushed to such a degree that the quality of the pitch became quite unacceptable from a wetting behaviour point of view as we will see later. The decrease in production of coal briquettes using soft pitch urged distillers to utilize more modern

distillation units where electrode binders are produced on-line from tars (straight-run pitch).

Although the description of the different designs of distillation features are beyond the scope of this paper, it would be interesting to review these in detail and to address the effects of design and operations on pitch quality. A typical scheme of a tar distillation unit is presented in figure 2. [14] It has the advantage of simplicity as it is quite similar to the principle applied to crude oil distillation. In the first atmospheric step on top of the fractionation column, at a low-boiling point (BP 80 – 200 °C) the light oil is removed. A blend of chemical carboic oils is extracted in the mid area at boiling ranges between 180 – 210 °C. The heaviest removed fraction, boiling between 210 – 220 °C, is the naphthalene oil (one of the main constituents of the liquid fractions) and thereafter, some light wash oil boiling from 230 – 250 °C.

The so-called topped tar that represents about 80% of the crude tar is then slightly heated to a temperature level of 320 °C and enters the vacuum (100 hPa or mbars) distillation unit where the heavy wash oil (BP 260 – 290 °C) and the main fractions of anthracene oil (up to 25% of the tar) are produced (BP between 300 – 450 °C under atmospheric pressure).

The conditions of distillation are selected to produce pitches with appropriate softening points or alternatively, to obtain a relatively low softening point pitch corresponding to the minimum value requested by some customers. Higher softening point pitch can be produced in a separate deep vacuum installation that avoids overheating (< 350 °C) of the pitch. To better understand the effects of heating/distillation on the tars a review on the properties of materials is essential.

Qualities of Tars and Pitches

It is estimated that tars contain up to 10'000 organic compounds. Despite a number of methods available [15] to identify 500 of these, there are so many reactions occurring during distillation that detailed analytical determination of compounds is impractical.

Due to the fact that higher molecular weight polyaromatic compounds provide high carbon yield after baking, while the lower molecular weight alkylated compounds with low C/H ratio are contributing factors to the low viscosity level needed for mixing the pitch with dry aggregate, various efforts for quantifying the type of "resins" present in tar and pitch were previously done by using different solvents. [16]

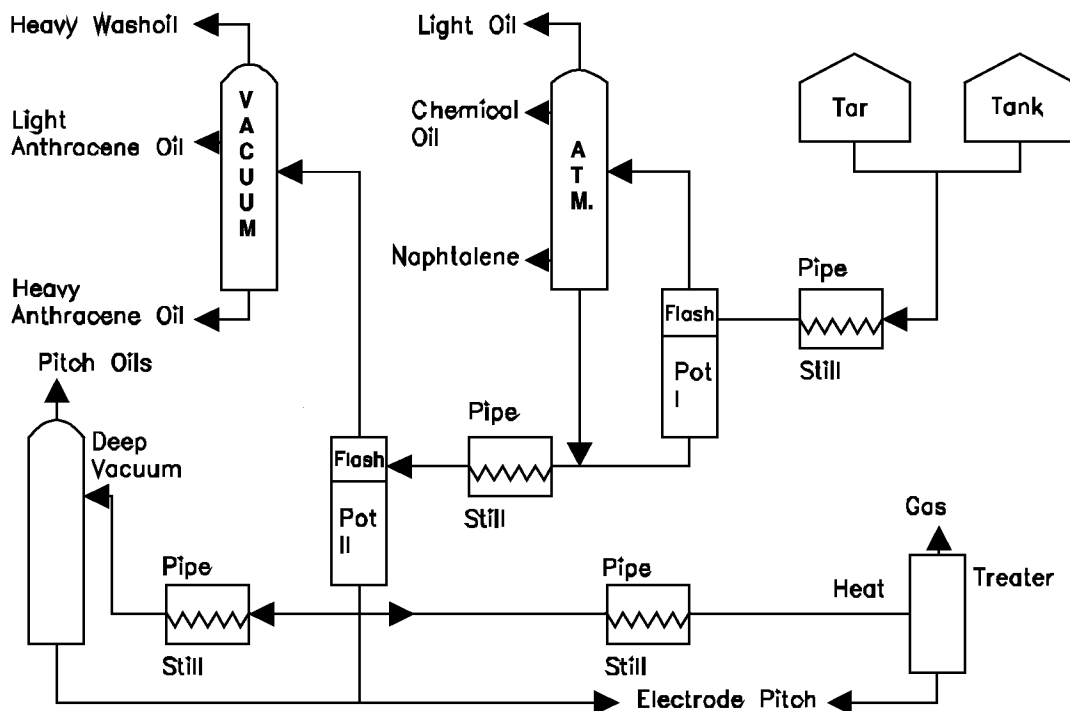


Figure 2: Possible scheme of tar distillation

Today, by applying Size Exclusion Chromatography (SEC), sometimes referred to as Gel Permeation Chromatography (GPC), it is possible to measure the molecular weight distribution. [17] This method is based on the selective retardation of the dissolved tar/pitch molecules due to their different degree of penetration into the pores of a gel matrix (stationary phase) filled with the same solvent. The material dissolved in quinoline is injected into a column which is eluted with the same solvent; molecular weights are determined with calibrated mass responsive detectors on collected fractions that are later distilled off at a reduced pressure in order to determine their respective percentage of the original pitch weight. This research method has the merit of not only showing the transformation of the tar into a soft pitch, but more importantly of the soft pitch into electrode pitch under more severe distillation/temperature conditions. This is shown in figure 3.

The removal of lighter volatiles from the tar which results in soft pitch leads to a proportional enrichment of the medium and high molecular weight components. However, polycondensation and polymerization reactions occur at the highest temperature range creating new medium and high molecular weight compounds of a different nature. This transformation can also be followed by examining the evolution of the insoluble fraction. From the numerous solvents with different strengths used by different schools [18], two remain well favoured, namely the quinoline and toluene insoluble. Although pitch molecules may have the same molecular weight components, their solubility to a given solvent may differ dramatically due to different molecular arrangement [19]. However we can say as a rule of thumb that:

- quinolene insoluble (QI) has a high molecular weight, above 3'000

- toluene soluble (TS) has a molecular weight below 1'000

Thus, the molecular weight compounds (1'000 to 3'000) are represented by the TI-QI fraction, commonly known as β resins. Table 1 shows the evolution of a typical tar when distilled to obtain a soft pitch and later, an electrode pitch using distillation or heat treatment. [20]

Frequency (%/100 m. w.)

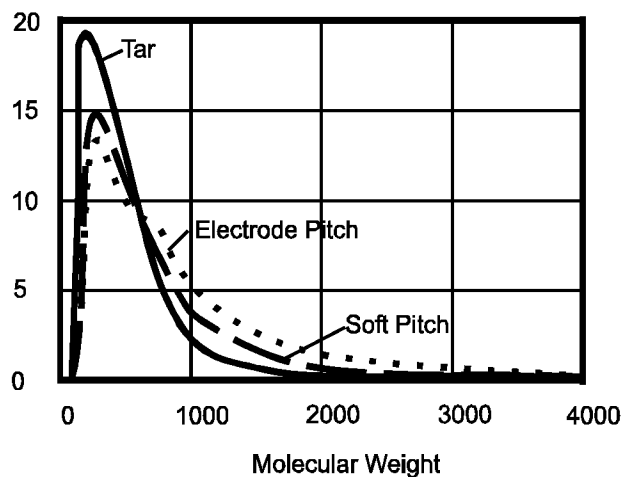


Figure 3: Molecular weight distribution of tar, soft and electrode pitch

Table 1: Properties of coal tar and of corresponding pitches

Properties	Unit	Tar	Soft Pitch	Electrode Pitch	
				Vacuum	H-T
Yield	-	100	53	45	46
Specific gravity	kg/dm ³	1.18	1.28	1.32	1.32
Coking value	%	20	43	58	59
C/H mol.	-	1.5	1.7	1.8	1.8
Quinoline insoluble	%	3	7	9	15
Toluene insoluble	%	8	18	31	38
Softening point Mettler	°C	< 0	85	112	112
Viscosity 160 °C	mPas	< 10	190	1600	1900

H-T: Heat-Treated

As distillation of tar is extended to the electrode pitch, there is an increase of density and coking values as the remaining components show lower hydrogen content. The increase in softening point and viscosity and the rise in quinoline insoluble are practically proportional to the ratio of tar/pitch yield for soft and vacuum electrode pitch. The TI content, however, increases in excess proportion in the vacuum pitch. This is an indication of the formation of β resins during distillation. [21]

In heat-treated pitch, there is a remarkable increase of QI due to the extreme high temperature conditions. This corresponds to the growth of the so-called mesophase [22] spheres that are visible through polarized light microscopy on the polished pitch specimen and also with scanning electron microscopy done on filtered QI from the treated pitch.

The 1 μ m size carbon black particles formed in the coke oven, the so-called primary QI, only have hydrogen speckles present on the periphery. On the contrary, mesophases named secondary QI contain more hydrogen [20] (C/H of 2 versus 4 for primary QI) and are generally one order of magnitude larger as they coalesce during heat-treatment. The presence of a certain percentage of large mesophase of about 50 μ m hinders the wetting and penetration of pitch in the fines and is therefore not desirable for anode manufacturing as pitch demand increases substantially.

This type of pitch practically disappeared in the eighties [14] but we have to keep in mind that heat-treatment was extensively used in Europe to fulfill the old QI specifications during the transition period of massive primary QI drop in tars to the modernization of the cokeries.

Table 2: Petroleum based tar and electrode pitch

Properties	Unit	Petroleum Tar	Electrode Pitch
Specific gravity	kg/dm ³	1.08	1.24
Coking value	%	8	50
C/H mol.	-	0.85	1.4
Quinoline insoluble	%	0	0.5
Toluene Insoluble	%	0	10
Softening point Mettler	°C	< 0	122
Viscosity 150 °C	mPas	< 10	1800

For petroleum pitch table 2 shows that the tar contains no insolubles and all indicators of aromaticity/severity of treatment are low. The corresponding electrode pitch distilled to a higher softening point target still guarantees the same viscosity although it shows a much poorer coking value. [23] Unless subtil interaction occurred during the blending of petro and coal tars, [24] the corresponding extended pitch will show a drop of QI, β resins and coking value.

Pitch Quality and Anode Performance

There are basic statements that can be made to define the preferred binder for prebaked anodes:

- A good wetting behaviour is guaranteed with a binder free of large mesophase showing a viscosity level that is in phase with the dry aggregate preheating and mixing capabilities.
- Exudation of pitch during the first stage of baking, which leads to packing material sticking and anode gluing, is more intense with binder prepared out of low severity/aromaticity tars. [25] In this instance, a lower pitch content will be required with such a binder in order to produce acceptable anodes.
- Macrocrack formation during baking is related to the too rapid release of volatiles which in turn leads to a too steep heat-up rate. A low and smooth (distillation) loss of pitch is needed to provide consistency in mechanical strength and resistivity of the anode.
- In the same line, a low baking loss/high coking value guarantees good anode density, permeability and strength level. [26, 27]
- The negative impact of excess sodium in anode burning has been extensively studied and proven. [10, 28] Therefore, the measurement of chlorine and Na content in tar and pitch allows for a better control of the appropriate neutralization process.

Concerning other controversial aspects of pitch aromaticity and the binding β resins (middle molecular weight compounds) we can summarize as follows:

- Very low aromaticity/low carbon black content pitch shows good wetting properties, but as the pitch content is limited by the exudation issue and the coking value is lower, an adaptation of the dry aggregate fines is mandatory in order to maintain anode quality. [1]

It has to be emphasized that the lower baking loss of high carbon black content pitch is not only related to the high coking value of this fraction. The remaining 85 to 90% of the pitch also shows a significantly higher coking value [29] even if the content in middle molecular weight compounds is similar. This illustrates the limit of solvent analysis of pitch.

- As observed in the agglomeration of coal briquettes several decades ago, the compounds, bounded with high β resins pitch had better **green** strength, an aspect that is not very relevant for green anodes.

For the final electrode, it was observed that for graphitized products, lower resistance was obtained due to better graphitizability of the β resins. However, for the amorphous (1100 °C) baked product, no difference was observed. [30] Therefore, any optimization or fine-tuning of the atmospheric/vacuum distillation to produce higher β resins is not based on solid arguments. [31, 32]

WORLD WIDE PITCH CHARACTERISTICS

Analytical Characterization

Based on performance requirements, many methods have been developed for analysis [33] and some that address the consistency aspect have been standardized and are well utilized throughout the industry.

Table 3 below summarizes the most acceptable ISO methods used for analyzing pitch when traded between continents. A brief summary of the analytical procedure is given in the appendix. Amongst the methods that are at times stated in the specifications by Al-groups to pitch suppliers, the following are worth mentioning:

- Mesophase content
- Penetration temperature tests
- C/H
- C/H of QI
- Coking value of β resins

These methods are considered interesting for product development and research purposes, like C_{13} NMR and SEC, but are not suitable for routine quality control at Smelters.

Table 3: ISO methods for routine quality control and typical range of pitch (2001)

Properties	Unit	Method	Typical Range
Softening point Mettler	°C	ISO 5940	110 - 115
Insoluble in quinoline	%	ISO 6791	6 - 16
Insoluble in toluene	%	ISO 6376	26 - 34
Viscosity 160 °C	mPas	ISO 8003	1200 - 2000
Density in water	kg/dm ³	ISO 6999	1.31 - 1.33
Coking value	%	ISO 6998	56 - 60
Distillation 0 - 270 °C	%	ISO N647	0.1 - 0.5
0 - 360 °C	%	"	3 - 6
Ash content	%	ISO 8006	0.1 - 0.3
S	%	ISO 10238	0.4 - 0.6
Na	ppm	ISO 12980	50 - 250
Cl	ppm	"	50 - 150
Ca	ppm	"	20 - 100
Si	ppm	"	50 - 200
Fe	ppm	"	50 - 300
Zn	ppm	"	100 - 500
Pb	ppm	"	100 - 300

WORLDWIDE PITCH QUALITY

In 2001, an extensive review was conducted on pitches produced by three-quarters of the total producers in the western world. As shown in figure 4, there is a general consensus on pitch softening point level as two thirds of plants operate within a narrow temperature range between 110 – 115 °C.

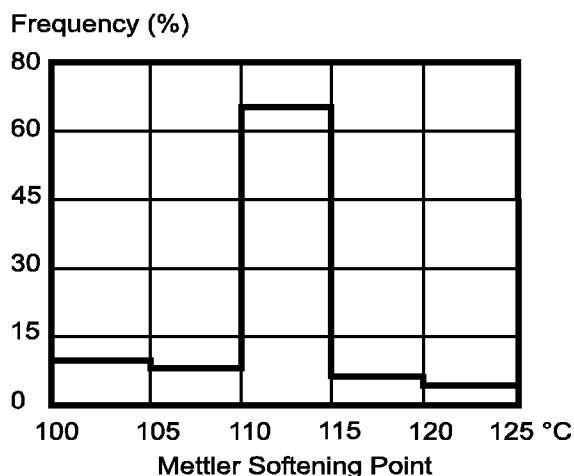


Figure 4: Distribution of Mettler Softening point of pitches used for prebaked anodes

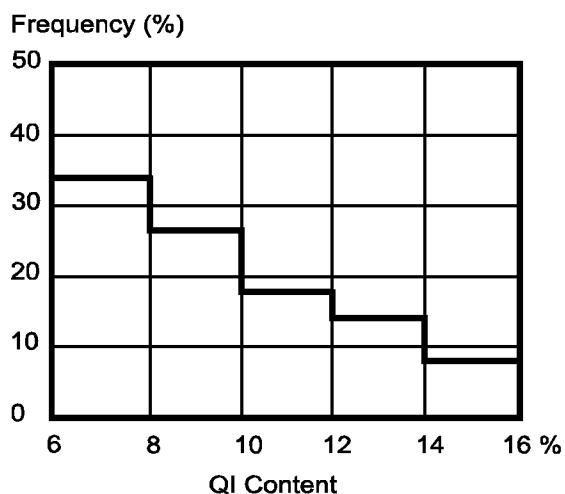


Figure 5: Distribution of QI content of pitches used for prebaked anodes

The quinoline insoluble distribution (Figure 5) is quite asymmetrical with the most frequent class lying between 6 to 8 % QI. A decade ago, a two-peak distribution was typical [34] but today, with the closure of old cokerries and the blending of tars in the US, high QI pitches are receding. For the minimization of odour emissions improvements have been made to the coke ovens. Better control of the charging step allows for a consistent high filling degree of the chambers. For trouble-free coke oven operation and by-product treatment, tars with a QI value of less than 2 % (4 – 5 % in pitch) are considered ideal. [5]

From the last decade, the QI range has been widening and this phenomenon will continue due to the introduction of < 5 % QI pitch on the market. It is envisaged, however, that within two decades there will be no pitch with QI > 10 %. If we filter out the data of extreme pitches related to carbon plant peculiarities, a typical range of pitch may be defined as shown in table 3.

Interrelationship of Pitch Properties

Prior to reviewing the specification aspects of pitch it is important to remember that most of the properties mentioned in table 3 are interrelated [35, 36]. Some links, like softening point and viscosity are more perceptible and to a given degree, the link between QI and TI.

The most important fact to remember is that changing the softening point target will impact on all characteristics (even on purity); the same would apply if the QI would need to be lowered in order to follow the tar trend. Of course, in the latter an adaptation to the softening point would be an appropriate method of compensating for the drawbacks.

Table 4 gives some insight on the effects of both key properties on other characteristics for a typical pitch. The increase of softening point and the decrease of QI have been considered as these relate to trends observed in industry.

Table 4: Effects on softening point and QI changes on the pitch characteristics

Properties	Unit	+ 1 °C SP	- 1 % QI
Softening point Mettler	°C	(+ 1)	0*
Insoluble in quinoline	% rel.	0.7	**
Viscosity 160 °C	% rel.	20	-3
Coking value	% abs.	0.2	-0.3
Density in water	kg/dm ³	0.001	-0.002
Toluene insoluble	% rel.	1.0	-5
Distillation 0 - 270 °C	% rel.	-5	***
0 - 360 °C	% rel.	-3	***
Ash/Elements	% rel.	0.7	****

* assumed to remain a constant target
 ** -1 % abs. by definition
 *** values too low to be considered
 **** depends on the cokery/tar

Specifications

Good specifications relate to and are based on paste producer and user experiences. The user has to define the level of softening point that is appropriate to his process; this is the only key property that is intensively monitored in the statistical process control (SPC) system of the distillers.

The stability of other characteristics is highly dependent on the tar blending and logistics aspects. The efficiency of the system can be measured by analyzing the incoming and used tars especially for QI content as this value should be maintained constant to avoid instabilities in the carbon plant and inconsistency in anode quality.

In order to define the specification range for the softening point, one has to firstly consider the guaranteed range that the distiller has provided over the last year and progressively reach a range of 4 °C or lower by means of classical SPC tools (see figure 6). A further reduction of the range or other properties may be negotiated yearly. This is based on the assumption that the quality consistency achieved will be maintained in future, unless major changes occur especially in tar supply.

In this case, it is strongly recommended to anticipate the new situation by conducting trials that reveal the carbon anode process adaptation required for the successful usage of the new binder with a different softening point target. Specifications are then tentatively redefined based on former variability information until more factual specifications are made available with new deliveries.

Softening Point Mettler (°C)

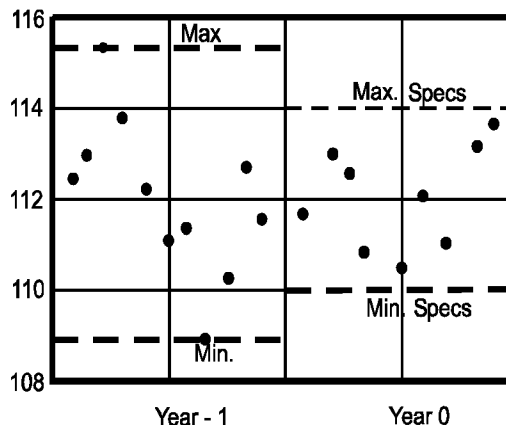


Figure 6: Choosing pragmatic specifications range and squeezing them progressively

Pitch Evolution

The average pitch softening point has increased by about 10 °C over the last 3 decades. The logical request for higher coking value binder can be coped with by the user by adapting mixing and forming processes and by producers through improvements of the distillation units. A couple of years ago pitch with Mettler softening point higher than 120 °C has been developed mainly for the reduction of PAH emissions in Söderberg smelters. [12] These pitches can be used by newly constructed prebaked anode plants with the proper design of preheaters and by using liquid pitch, which, due to hygiene concerns, will eventually replace solid pitch.

An interesting point is the drift in quinoline insoluble that dropped in Europe during the eighties by 50 % rel. and also in North America in the late nineties with the usage of petroleum streams

that replaced the depleted local high QI coal tar. Massive imports from former eastern block countries eased the changes in Europe but it is anticipated that within two decades most pitches will show QI content around 5 %.

CONCLUSIONS

The right response from the Al industry to the abovementioned trend is to fully adapt the green mill from a thermal and fines preparation point of view.

Pitch producers and users have learnt from past experiences not only which errors have to be avoided with the changing conditions in the tars and in end-product demand, but also in selecting the right approach for efficient adaptation of the entire manufacturing chain. [37]

Research and development tools are available to guide and anticipate the changes to come. With systematic routine quality control the consistency of the pitch can be improved.

Both tools, together with a sound knowledge on the different topics, from aromatic chemistry to the physical interaction in green paste or electrode baking production, are the key issues for a successful reduction of the Aluminium production cost, and these are also of benefit to the tar distillers.

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APPENDIX: ISO METHODS FOR PITCH

The ISO standard methods may be purchased by contacting the national standardization bodies directly, or, from the ISO homepage:

<http://www.iso.ch/iso/en/ISOOnline.openerpage>

ISO 6257 Sampling

This vital step in analysis and testing is well described in this standard. It gives precise information on the sampling plan, the procedure for selection, withdrawal and preparation of samples from a given lot. Guidelines to determine the quantity of material to be sampled from anticipated monthly deliveries are given together with the number of samples which should be taken.

Sampling tools and devices are described for solid and liquid pitches.

ISO 5939 Water Content

A standardized method used for the azeotropic distillation of water that may be present in solid pitch. A representative crushed sample <8 mm is placed in a flask with 250 ml xylene and heated to boiling point. The vapours are condensed and the water is separated from the xylene due to the water's low solubility at room temperature.

The quantity of water is read off a graduated glass receiver and the result is calculated in %.

ISO/TC47/SC7 (CH-106) N647 Distillation Analysis

A distillation flask with a side outlet cooler tube is used to distill a pitch sample of 100 grams (< 8 mm). The distillation temperature of the vapour is measured with a thermometer mounted on the upper part of the flask.

An electrical heater is used; the distillation time period range is defined and the power is selected accordingly. Two fractions of distillate, up to 270 °C and 360 °C are collected and weighed. The results are given in % and are rounded off to the first decimal place. An ISO 12977 method using a gas chromatograph as an alternative is currently being prepared.

ISO 5940-2 Softening Point Mettler

ISO SC7 has recently started standardization work on this well-known method. (See also ASTM D3104-82 or DIN 51920.) The softening point is defined as the temperature at which pitch, placed in a cylindrical cup with a ¼ inch hole at the bottom, flows downward for a distance of 19 mm whilst the sample is heated at a linear rate in air.

A 1 gram pitch fraction (1 – 2 mm) is pressed into a standardized dimension cup. This is placed in a cartridge that is heated up in a furnace at 2 °C/min. A molten pitch droplet interrupts a light beam when passing through slits made in the cartridge receiver. The result is given to the nearest 0.1 °C by an automatic control unit.

ISO 8003 Dynamic Viscosity

This standard describes two methods. The first method uses (DIN 52007) a ball drawn by a defined force while the second uses a revolving body. (See also ASTM D4402.) Here the torque of a spindle rotating in a special thermostatically controlled sample holder containing a small sample of molten pitch is measured.

The dynamic viscosity in mPas is usually measured at a temperature of 160 °C.

ISO 6999 Determination of Density – Pyknometric Method

The measurement is made with water. A standardized Gay-Lussac pyknometer is used; 5 grams of 1 – 2 mm pitch sample is introduced and the unit is assembled into a glass container that has a separating funnel with a stopcock.

A vacuum of 35 mbar is applied and water from the separating funnel is introduced into the pyknometer. The pyknometer is then filled completely with water and placed into a water bath at 25 °C. The density is calculated by weighing the pyknometer at a temperature of 25 °C. The result given in kg/dm³ is rounded off to the third decimal place.

ISO 6998 Determination of Coking Value

A pitch sample is heated at 550 °C for 2.5 hours and the residue is weighed. A test portion of 1 gram of sieved pitch <0.25 mm is placed in a porcelain crucible that is then inserted into a larger nickel crucible filled with calcined petroleum coke to avoid oxidation. A rack is used to prevent the nickel crucibles from touching the bottom of the muffle furnace.

The mean value of four results as a percentage of mass is given to the nearest 0.1 %.

ISO 6791 Determination of Content of Quinoline-insoluble Material

A pitch sample is extracted with quinoline and the insoluble is then filtered. A test portion of 1 gram of sieved pitch < 0.25 mm is introduced into a conical flask with 25 ml of quinoline. After heating up to 80 °C the contents are occasionally stirred for 15 minutes. With suction, it is then filtered through a glass fibre filter pad using hot quinoline followed by hot toluene to rinse off the glassware and wash the residue. After drying and cooling the filter, the residue is expressed as a percentage of mass rounded off to the first decimal place.

ISO 6376 Determination of Content of Toluene-insoluble Material

An extraction of a pitch sample is made with toluene followed by filtration of the insoluble. A test portion of 1 gram of sieved pitch < 0.25 mm is placed into a 500 ml conical flask with 100 ml hot toluene. A reflux condenser is used to condense the boiling toluene for 30 minutes.

The contents are sucked through a filter crucible that contains a sintered glass disc or alternatively by using a glass fibre filter pad. After drying and cooling the filter, the residue is expressed as a percentage of mass rounded off to the first decimal place.

ISO 8006 Determination of Ash Content

A test portion of pitch placed in a crucible is heated slowly in a furnace up to a temperature of 700 °C under an oxidizing atmosphere until the mass is constant.

Alternatively the coking residue of the ISO 6998 method can be utilized. A 2 gram sample is usually burnt for 6 to 12 hours and the residue is expressed as a percentage of mass rounded off to the second decimal place.

ISO 9055 Sulfur content – Bomb Method

A test portion is oxidized in a bomb under pressure containing oxygen. It follows a gravimetric determination of the sulfur as barium sulfate.

ISO 10238 Sulfur Content – Instrumental method

A known mass of the sample is burnt into a stream of oxygen at a temperature of 1350 °C. The oxides of sulfur together with any chlorine present are absorbed by neutral hydrogen peroxide and determined volumetrically. A correction is made taking into account the chlorine content of the sample. The method is applicable to coal and petroleum pitch.

ISO 12980 Analysis of Elements – XRF Method

This method, originally developed for coke, can be used for pitch with minor adaptation for sample preparation. For pitch, no binder is needed to prepare a tablet, with a < 0.25 mm sieved pitch sample, using a press.

This pressed tablet is irradiated by x-rays from a thin window tube. Irradiation of the sample causes ejection and the rearrangement of orbital electrons occurs, resulting in the emission of secondary radiation with a characterized wavelength for each element. The secondary radiation is refracted by a crystal, which is set at a certain angle to the radiation. Only specific radiation, which obeys Bragg's law reaches the detector system.

The intensities of the specific secondary radiation are calculated into concentrations according to given calibration curves obtained with standards (see ISO 14435 for flame atomic absorption spectroscopy or ICP methods on coke). Results are reported in ppm for Si, Fe, Na, Ca, Ce, Pb and Zn and in % for S.