Development of Soderberg Carbon Electrodes Bonded with a Carbon Nanofibre Reinforced Coal-Tar Pitch

J. R. Campello-García, D. Castaño-Laviana, M. Miranda-Martínez

The operation of Electric Arc Furnaces (EAF) relies on the use of different types of carbon electrodes. Most of them are subjected to thermal treatments before use. However, Soderberg electrodes are formed in situ. Their carbon paste is fully transformed under operation. Soderberg paste is composed of calcined anthracite and petroleum coke, pitch being used as binder. This work evaluates the incorporation of Carbon Nanofibres (CNF) to coal-tar pitch for Soderberg paste production. The effects of this nano-addition have been studied both on the coal tar pitch alone and on the Soderberg paste mix. To carry out the study a reference formulation, composed of coal tar pitch, calcined anthracite and petroleum coke, was designed, processed and characterised.

1 Introduction

Soderberg type electrodes were developed in 1917 by Elkem/NO. They have been used in submerged Electric Arc Furnaces (EAF) and other electrode based furnaces [1]. The thermal treatment of the Soderberg electrode paste takes place during the operation of the furnace [2, 3, 4]. Soderberg paste briquettes are fed at the top of the electrode and, by Joule effect, the paste is heated, softens and slips down, being at the same time progressively transformed into a conventional graphite electrode. During operation, the electrodes present four distinct zones (Fig. 1):

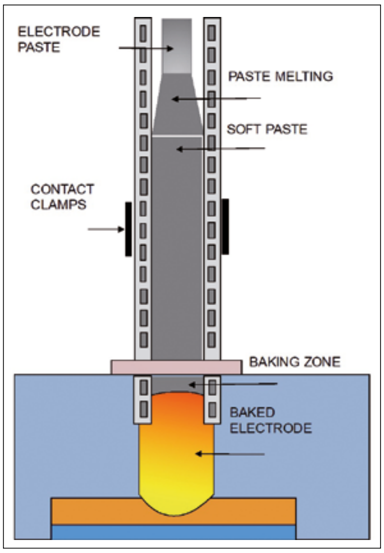

Fig. 1 Scheme of a Soderberg type electrode (adapted from [5])

- an upper one where paste is in green state;
- a zone where a coke or semi-coke is being formed;
- a third one where the paste has been completely coked; and, finally,
- a lower one where the paste has completely graphitized becoming a conventional graphite electrode.

At each zone, the required properties of the Soderberg paste are different. In zone 1 the flow behaviour of the paste conditions its performance; if too fluid its components may segregate. Conversely, if too stiff it would lead to poor compaction.

In zones 2 and 3 the behaviour of the paste during carbonisation determines the mechanical properties of the coked electrode. In those zones a common cause of Soderberg electrode failure is hard fracture, occurring when an already coked volume of the electrode detaches from the rest of the piece [6]. This outcome is generally attributed to uncontrolled baking, which, even when not fatal, causes low mechanical strength.

Another highly relevant property of the paste is electrical conductivity. A lower resistivity could lead to a reduction of the furnace electrical consumption. In this research a close look has been taken at the influence of the introduction of Carbon Nanofibres (CNFs) in a coal-tar pitch, their influence on the pitch carbonisation process and rheology, and also on the mechanical and flow behaviour properties of a reference Soderberg paste processed with CNFs doped coal-tar pitch.

2 Experimental and results

2.1 Investigation of coal-tar pitch

The main difficulty in the development of nanoparticle reinforced composites is the proper dispersion of nanoparticles. For in-

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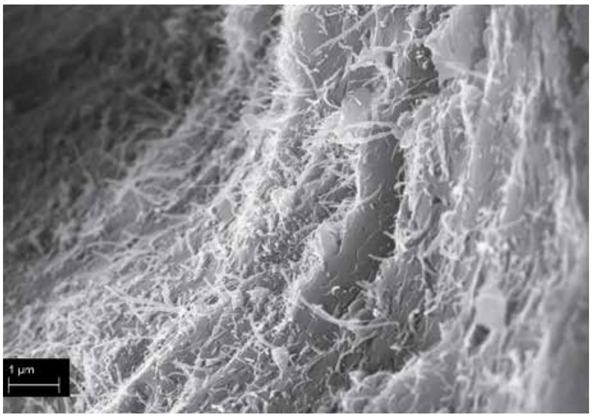

Fig. 2 **Detail of a CNF agglomerate in a CNF doped coal-tar pitch fracture surface**

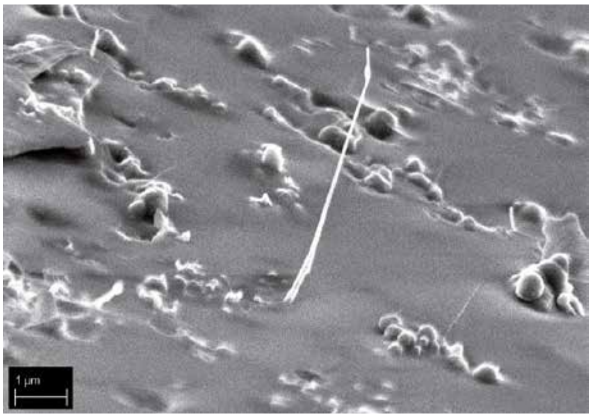

Fig. 3 **Detail of carbon nanofibres properly dispersed on the coal-tar pitch**

stance, carbon nanofibres tend to agglomerate forming tangles or cluster in the pitch. Carbon nanofibres dispersion was evaluated by scanning electron microscopy. Fig. 2 shows the result of a CNF dispersion trial where tangles of nanofibres can be seen on a fracture surface.

Optimal dispersion was obtained by carbon nanofibres surface functionalization before incorporation in the pitch, the latter being carried out under intense mixing. Fig. 3 presents an example of adequate dispersion of CNFs in the coal-tar pitches used in this investigation.

Coal-tar pitch basic properties, namely Mettler softening point (ASTM D3014), quinoline insoluble (ASTM D4746), toluene insoluble (ASTM D4072) and fixed carbon (ASTM D3172), were determined. Tab. 1 shows the values obtained. The addition of carbon nanofibres resulted in an increment in the softening point and fixed carbon value.

The effect of carbon nanofibres to the carbonisation of the pitch was evaluated under polarised light microscopy. For this purpose, pitch without carbon nanofibres and with a 0,2 % content were thermally treated at 1000 °C for 5 h (heating rate of 60 °C h^{-1}). The resultant coke was embedded in resin, polished and observed. Fig. 4 shows the microstructure of the coke without carbon nanofibres, while Fig. 5 shows the microstructure of the CNF doped coke. Figs. 6–7 present respectively the microstructures of un-doped and doped cokes when observed with crossed nicols and a wavelength retarder.

Tab. 1 **Properties of the coal-tar pitch un-doped and doped with CNFs**

	CNF Content [w/0]			
	0 %	**0,1 %**	**0,2 %**	**0,5 %**
Mettler softening point [°C]	69,0	75,0	74,3	84,5
Quinoline insoluble [w/0]	26,9	28,6	29,5	30,0
Toluene insoluble [w/0]	9,9	11,3	11,4	13,7
Fixed carbon [w/0]	48,7	51,5	51,1	52,5

Viscosities of un-doped and doped coal-tar pitch were determined by rheometry using parallel, 40 mm diameter plates, geometry (TA Instruments DHR-2). Two sets of experiments were carried out: i) at a constant shear rate, while increasing the temperature, and ii) at constant temperature, while varying the shear rate. Fig. 8 presents the viscosity of the coal-tar pitches at a constant shear rate of 10^2 s^{-1} while increasing the temperature from 100 °C up to approximately 180 °C at 5 °C min^{-1}. Viscosity increases significantly when carbon nanofibres are incorporated to the pitch.

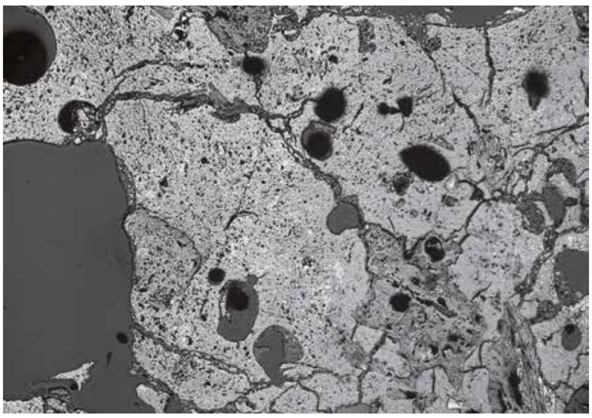

Fig. 4 **Microstructure observed by optical microscopy of the coke obtained from pitch with 0 % NFC (× 40)**

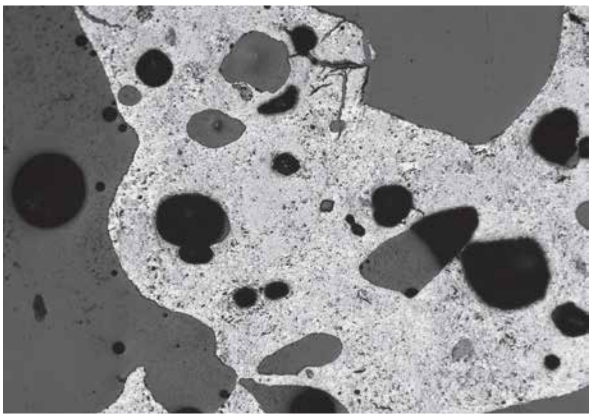

Fig. 5 **Microstructure observed by optical microscopy of the coke obtained from pitch with 0,2 % NFC (× 40)**

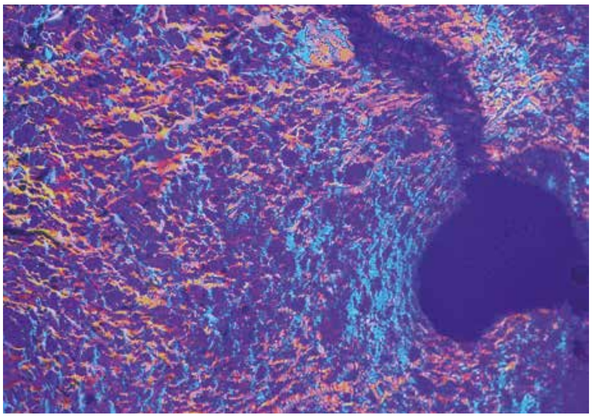

Fig. 6 **Microstructure observed by optical microscopy of the coke obtained from pitch with 0 % NFC (crossed nichols, × 200)**

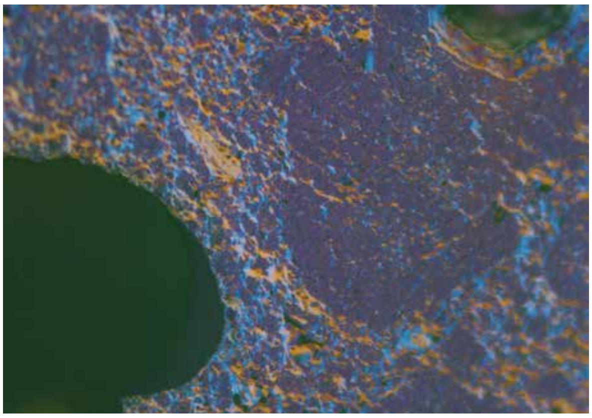

Fig. 7 **Microstructure observed by optical microscopy of the coke obtained from pitch with 0,2 % NFC (crossed nichols, × 200)**

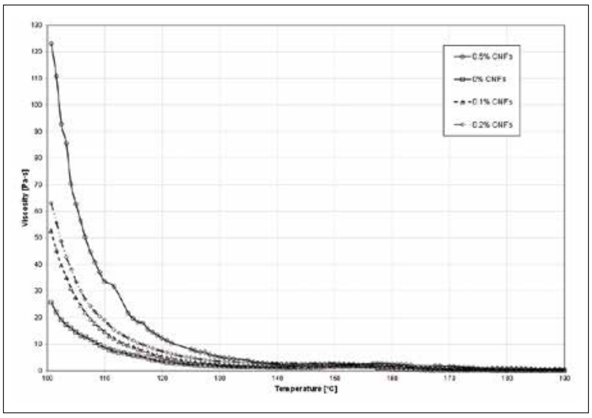

Fig. 8 **Viscosity versus temperature of the coal-tar pitches for a shear rate of 10^2 s^{-1}**

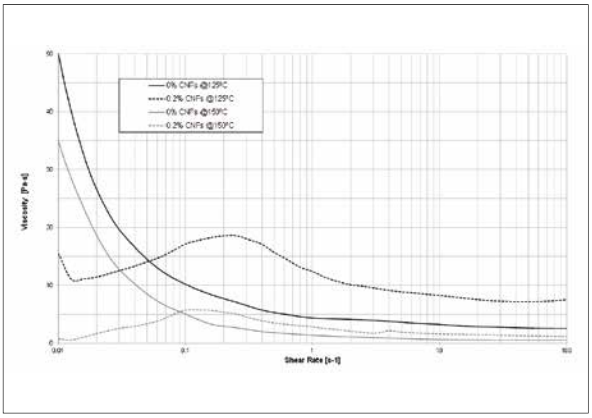

Fig. 9 **Viscosity of reference pitch and 0,2 % NFC pitch at 125 °C and 150 °C**

For instance at 100 °C the viscosity of the reference pitch is 26 Pa·s, 52 Pa·s for a CNF content of 0,1 % and 120 Pa·s for a 0,5 % content. Above 140 °C the pitches reach a viscosity about 10^2 Pa·s independently of their content in carbon nanofibres.

The dependency of the viscosity and shear rate for the reference pitch, and the pitch with a 0,2 % of carbon nanofibres is shown in Fig. 9. The curves were obtained at 125 °C and 150 °C and varying the shear rate between 10^{-2} and 10^2 s^{-1}. Under this conditions a clear dependency between viscosity and shear rate was observed. Shear rates higher than 10^1 s^{-1} resulted in an approximately constant viscosity for both CNF doped and un-doped pitch. For each temperature there is a critical shear rate, determined by the intersection between the curves for the doped and un-doped pitch. At shear rates higher than the intersection point the viscosity of the doped pitch is higher than that of the pitch without carbon nanofibres. To the left of such intersection the viscosity of the CNF doped pitch is significantly lower. To the right there is a transient viscosity hike for CNF doped pitch. The shear rate critical values are temperature dependent. For a 0,2 % CNF content in the pitch, critical values were 0,05 s^{-1} and 0,09 s^{-1} at 125 °C and 150 °C respectively. Below that critical shear rate value the doped-pitch would flow more easily than the un-doped one.

2.2 Investigation of Soderberg paste

A reference Soderberg paste formulation – containing coal-tar pitch, calcined anthracite and petroleum coke – was processed on a high intensity mixer (R08 Eirich/DE) to investigate the effect of different amounts of carbon nanofibres in the coal-tar pitch used as binder. Namely, 0 %, 0,1 %, 0,2 % and 0,5 % additions were tested. Tab. 2 shows the raw materials and range of compositions employed. Petroleum coke and calcined anthracite were preheated between 250 °C and 350 °C before mixing in order to increase the temperature of the mixture above the pitch softening point. Once mixed the paste was cast into metallic moulds, vibrated for 60 s and cooled with tap water.

The electrical resistivity of the Soderberg paste was measured after thermal treatment at 900 °C. CNFs additions resulted in a reduction of electrical resistivity from 81 µΩ · m, of the un-doped paste, to 64 and 47 µΩ · m for 0,1 % and 0,2 % additions respectively.

Flexural strength of the paste was determined according to EN 993-6 in crude state and after thermal treatment at 500 °C and

Tab. 2 **Raw materials and range of compositions for the reference formulation**

Raw Material	Range [w/0]
Coal-tar pitch	20–30
Calcined anthracite	35–50
Petroleum coke	25–40

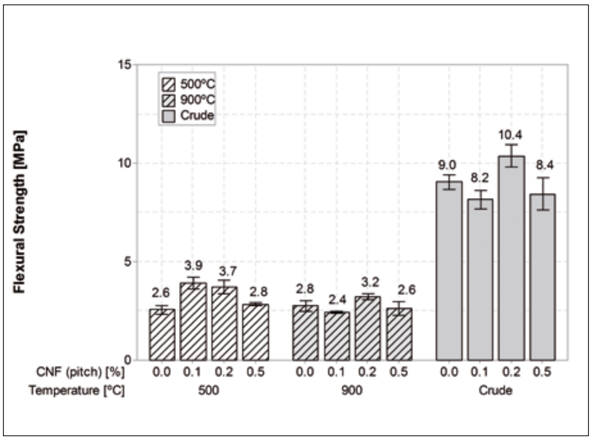

Fig. 10 Flexural strength of reference Soderberg paste in crude state and after thermal treatment as a function of CNF in the pitch

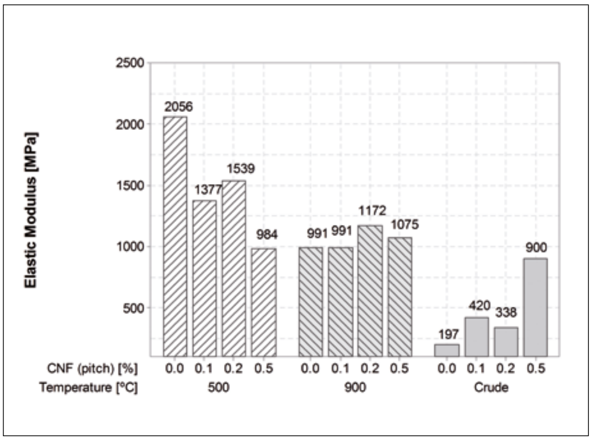

Fig. 11 Elastic modulus of the reference Soderberg paste in crude state and after thermal treatment as a function of CNF in the pitch

900 °C for 5 h (at a heating rate 30 °C h^{-1}). Cylindrical stainless steel moulds (300 mm height and 150 mm diameter) were used to contain the paste. After thermal treatment no component segregation of the Soderberg paste was observed.

Fig. 10 shows the flexural strength of the reference paste. A reduction of mechanical properties after thermal treatment was observed which is attributed to the release of volatiles during the carbonisation process. After thermal treatment at 500 °C 0,1 % and 0,2 % CNFs additions in the pitch resulted in increased flexural strength, up to 50 % compared to un-doped paste. Nevertheless, higher CNFs contents resulted in strength values close to those of the un-doped paste.

The elastic modulus of the reference Soderberg paste was also calculated from the linear range of the stress-deformation curves from flexural tests. Fig. 11 depicts the Young's modulus of the Soderberg paste in crude state and after thermal treatment. In the case of crude pastes, an increment in the elastic modulus with the CNF content was determined. The values went from 200 MPa to approximately 1 GPa. This behaviour is attributed to the high stiffness values characteristic of carbon nanofibres [7–9].

After thermal treatment at 500 °C an opposite trend was observed, that of an elasticity reduction from about 2 GPa, for the un-doped paste, up to approximately 1 GPa, for a 0,5 % CNF content in the pitch. However, once the paste was treated at 900 °C there was no effect of carbon nanofibres in Young's modulus in the paste.

The flowability of the reference Soderberg paste was measured using cylindrical test specimens 50 mm height and 50 mm diameter, shaped by pressing. The specimens were heated to 305 °C for 1 h , at a heating rate of 60 °C h^{-1}, while resting on a graphite paper. The action of heat on the coal-tar pitch slowly softens the Soderberg paste which flows under its own weight.

Thus, flowability was calculated from the initial (d_0) and final diameters (d_f) of the test specimens as $FV = 100\ (d_f - d_0) / d_0$. Fig. 12 shows the values, obtained as the mean value of five determinations, plotted versus the CNF content in the coal-tar pitch. Flowability of the reference paste was about 56 %, increasing to more than 70 % for 0,1 % to 0,2 % CNFs in the pitch. However, at a 0,5 % CNFs content, a striking flow reduction was observed, the values falling about 66 %, although they were still higher than of the un-doped paste.

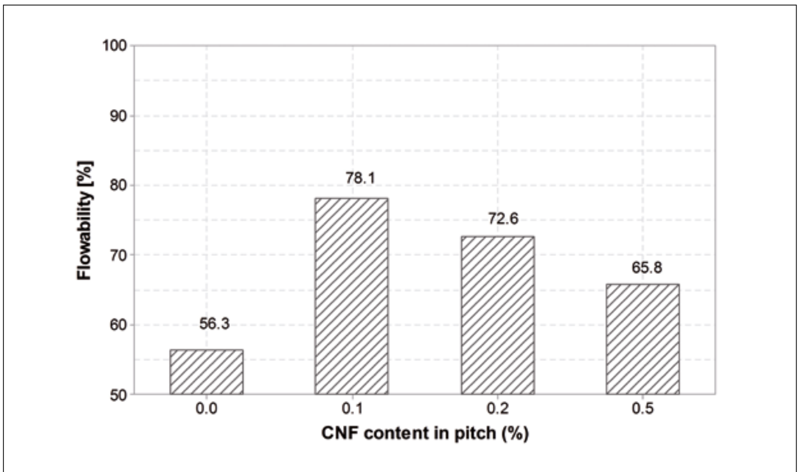

Fig. 12 Flowability results for a Soderberg paste as a function of CNFs content in the coal-tar pitch

3 Discussion

The results obtained in the flowability tests reveal an increment in the flow in the pastes with up to a 0,2 % CNFs content in the pitch used as binder. When the CNFs content is increased up to 0,5 % a reduction in the flow is observed, although it is still higher than for the un-doped paste.

In these tests, the flow of the paste is due to the effect of its own weight and the progressive increment in temperature. According to this fact the shear rates in the test are low, namely between 10^{-2}–10^{-1} s^{-1}. At industrial scale Soderberg paste is fed in the form of briquettes, compacted and, as long as the graphitized electrode is consumed, slips down less than 1 m per day [2]. According to this the shear rates involved in this process are also low. Under these conditions the carbon nanofibres have a thinning effect, reducing the viscosity of the pitch and easing the flow of the Soderberg paste. The further thickening effect of the carbon nanofibres in the pitch have also a positive effect: at a higher shear rate this would reduce the segregation of the paste.

The rheological behaviour of the doped pitch is attributed to the internal structure provided by the carbon nanofibres due to their high length diameter ratio. At low shear rates the nanofibres are forming structures allowing the pitch's flow. When the shear rate increases the CNFs are entangled resulting in an increment in the resistance to the flow. Once the shear rate is increased even more the structure would become ordered again, permitting the flow of the pitch and reducing the viscosity.

The carbonisation process of the pitch is the modification of its structure under the action of temperature. It advances through the formation of a mesophase (a nematic crystal liquid) and, with a strong shrinkage, the transformation into a coke or semicoke [10–12].

When observed by optical microscopy the coke derived from the doped pitch has better accommodated this shrinkage, showing lower amounts of cracks and with a smaller size in comparison with the reference coke (Figs. 4–5). The observation with crossed nicols and a waveplate reveals the degree of anisotropy of the coke's microstructure. The microstructure of the coke formed from non-doped pitch was coarser than that of CNF-doped pitch, the latter showing a finer microstructure as CNF percentage increased. In the coke obtained from CNF-doped coal-tar pitch carbon domains are randomly oriented, having a higher degree of anisotropy.

This modification of the microstructure explains the improvement of the mechanical properties shown by Soderberg pastes containing carbon nanofibres after thermal treatment at 500 °C. Finer microstructure and a more anisotropic texture result in cokes exhibiting a higher mechanical strength [13].

4 Conclusions

Having in mind the key properties required for Soderberg electrodes:

- low electrical resistivity, in order to reduce the overall electrical energy consumption,
- high mechanical strength, but low stiffness, to reduce the risk of hard fracture of the electrode, and
- controlled flow behaviour, to avoid the segregation of the components of the paste, we can reflect that a significant improvement of its properties has been obtained for an 0,2 % CNF addition in the coal tar pitch used as binder in this study.

Electrical resistivity at 900 °C was reduced a 42 % compared with the reference paste, which should result in a reduction in electrical energy consumption. A reduction of the elastic modulus at 500 °C, and an overall increment in the flexural strength at 500 °C and 900 °C compared to a reference paste, were also measured. These values should lead to a better performance regarding the cases of hard fracture during operation, and therefore increase electrode average lifetime. The improvement of these mechanical properties has been attributed to the microstructural modification of the mesophase during the carbonisation of the doped coal tar pitch.

CNFs additions to Soderberg pastes resulted also in increased flowability, achieved without any segregation or poor compaction. This behaviour is thought to be explained by the effect CNFs on the rheology of the coal tar pitch since at low shear rates, characteristic of the Soderberg paste coking process, an important reduction of the viscosity was observed.

This effect would explain the improved flowability of the paste. Nevertheless, at higher shear rates (or temperatures) a transient increase in pitch viscosity would avoid the segregation of paste components. Once engineered such behaviour could be used to adjust the flow of the Soderberg paste, for instance allowing a reduction of pitch content, after all it's the most expensive component.

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