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The role of impregnants in determining the behaviour of graphite anodes

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The lifetime of graphite anodes in sulphuric acid media can be increased by a factor of 3.2 by multiple impregnation with coal tar pitch. For single impregnation, linseed oil yielded the largest improvement. The results were interpreted on the premise that properties such as viscosity, melting point and coking value determine the effectiveness of the impregnant. The proper selection of the impregnant and procedure of impregnation is dependent on the electrolysis temperature.

1. Introduction

Andrew and Distante [1] reported that the percentage change in graphite properties due to impregnation increased as the weight introduced into the pores went up. Mullina *et al.* [2] showed that the impregnant was distributed by capillary forces in the graphite pores. Sjodin and Wranglén [3] found that semiliquified linseed oil was more effective than completely solidified oil. Iro *et al.* [4], Kozar and Uveges [5], Maruyama and Nagaoki [6] and Zhirotovskii *et al.* [7] found that graphite anodes became more durable when repeated impregnation took place with compounds such as allyl resin solution, furfuryl resin, coal tar pitch and inorganic salts. Demitrieva *et al.* [8] reported that multiple impregnation with polyvinyl acetate emulsion improved the graphite anodes. Graham *et al.* [9] showed that such changes were due to charring of the impregnant, with subsequent precipitation of hard carbon in the pores.

The aim of the present work was to understand the role of such properties as viscosity, melting point and coking value in determining the effectiveness of the impregnant.

2. Experimental

2.1. *Materials*

2.1.1. The graphite anodes. The samples were prepared from petroleum coke and coal tar pitch. The procedure followed in the preparation is given elsewhere [10]. Samples with dimensions 70 mm x 40 mm x 8 mm were impregnated with linseed oil, paraffin wax, polyethylene A-wax and coal tar pitch containing 2% oleic acid according to the following procedure. The specimens were placed in thin-walled, mild steel containers with perforated bottoms. The containers were then heated under vacuum in the autoclave of an industrial impregnating machine. After 30 min, the liquified impregnant was sucked into the autoclave in a quantity sufficient to overflow the samples. Compressed air was then forced at 4 atm through a nonreturn valve for 1–4 h. The impregnation process was conducted at 80° C higher than the melting point of the impregnant. The impregnated samples were freed from extra impregnant by centrifuging while hot in an industrial machine, type M-72 Erhardt. The samples were then washed with nitrobenzene, benzene and finally with absolute alcohol and dried over P_2O_5.

2.1.2. The impregnants. Table 1 gives the technical specifications of the waxes, linseed oil and coal tar pitch used for impregnation.

2.1.3. Partial drying of the linseed oil. The local linseed oil was further dried by blowing air through it at 115° C until the required viscosity was attained. The process was conducted in a laboratory reactor.

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Table 1. Technical specifications of the impregnants

Property	*Waxes*		*Linseed oil**	*Coal tar pitch*
	Paraffin	*A-wax*		
Softening point (°C)	–	–	–	63 (K and S)
Free carbon (%)	–	–	–	45
Coking value (%)	–	–	–	40.3
Melting point (°C)	60–62	101–106	–	184
Penetration index	1	1–2	–	–
Specific gravity	0.94	0.91	0.943	1.12
Melting viscosity	650–800	850–1100	–	–
Acid value	–	–	8	–
Saponification value	–	–	97.4	–
Drying time (h)	–	–	18	–

* According to the Egyptian Standard 20-1958, 636.

2.2. *Determination of the corrosion rate*

The impregnated and nonimpregnated specimens were anodically polarized in 0.1–1.0 M H_2SO_4 at a constant current density of 50 mA cm^{-2} for periods ranging from 10–120 h. The perspex electrolysis cell, dimensions 25 cm x 18 cm x 15 cm, had a tightly fitting cover which served also as a support for the graphite anode, cathode, stirrer, heating arrangement, contact thermometer, pH probe, etc. The rate of wear of the graphite anodes was determined according to the method given by Wranglén *et al.* [11]. The error in weight loss values was ± 0.5%.

3. Results

Fig. 1. shows weight loss versus time (with constant current) curves obtained for graphite anodes in H_2SO_4 at 20° C. Similar types of curves were obtained at 50 and 75° C. It can be seen that the weight loss increases linearly with time and that the rates of both inner and outer wear increase with increase in acid molarity. Fig. 2 demonstrates the influence of the bath temperature on the anodic wear. It is shown that within the temperature range 20–75° C, both inner and outer wear decrease with rise in temperature [12].

Fig. 3 illustrates the relation between the rate of anodic corrosion and the weight of the impregnant inserted into the pores. It can be seen that for linseed oil, the rate of anodic wear decreases with progressive increase in the amount of impregnant. The curves obtained for paraffin wax and polyethylene A-wax display a minimum. For coal tar pitch, a constant rate of wear is approached.

Figs. 3 and 4 show that when the electrolysis is conducted at 20 and 50° C in 0.5 M sulphuric acid, the decrease in the corrosion rate is highest for linseed oil and lowest for the waxes. At 75° C, however, coal tar pitch is more efficient than linseed oil. Both are still more efficient than either paraffin wax or polyethylene A-wax (Fig. 5).

Table 2 summarizes the results obtained with

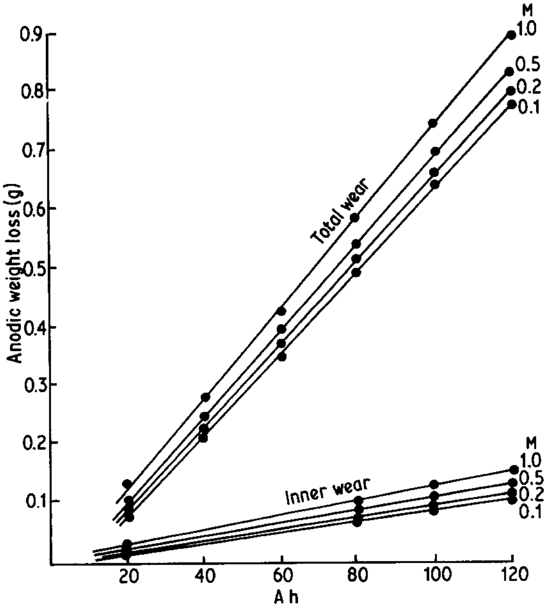

Fig. 1. Loss in weight versus time for nonimpregnated graphite anodes in sulphuric acid solutions at 20° C.

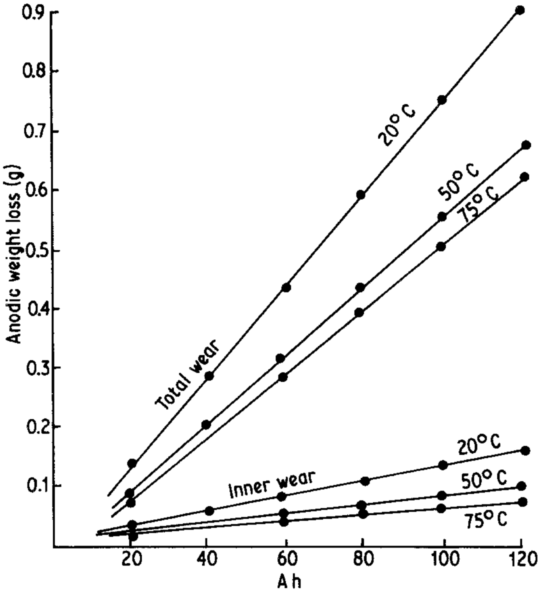

Fig. 2. Loss in weight versus time for nonimpregnated graphite anodes in sulphuric acid solution within the temperature range 20–75° C.

the different impregnants at the three temperatures. It is seen that the maximum weight of linseed oil that can be inserted into the graphite specimens (12%) reduces the corrosion rate by about 60% and 54% at 20° C and 50° C respectively.

Fig. 6 shows the influence of multiple impregnation on the corrosion rate of the graphite anode. The curves illustrate that the rate of anodic wear decreases linearly with the number of impregnations. It is interesting to note that the response to this kind of treatment is weakest in the case of linseed oil and strongest for coal tar pitch, the two waxes lying between. The decrease in rate of wear after the fifth impregnation (every single impregnation is followed by baking) amounts to 41.0%, 52.5%, 58% and 69.2% for linseed oil, paraffin wax, polyethylene A-wax and for coal tar pitch, respectively. These values correspond to an increase in the lifetime of the graphite anodes of 1.74, 2.10, 2.37 and 3.25 fold as compared with the nonimpregnated specimens.

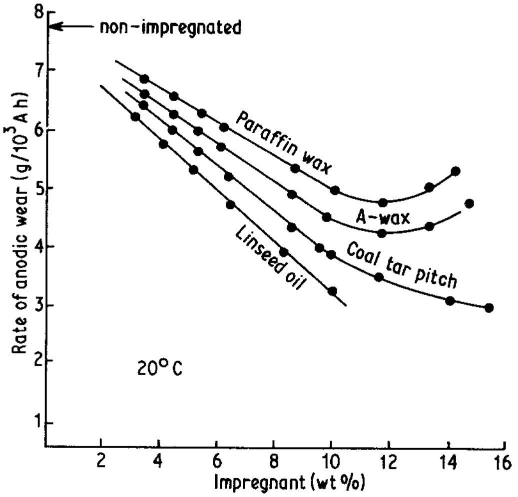

Fig. 3. Rate of wear versus weight per cent impregnant for impregnated graphite anodes in sulphuric acid solution at 20° C.

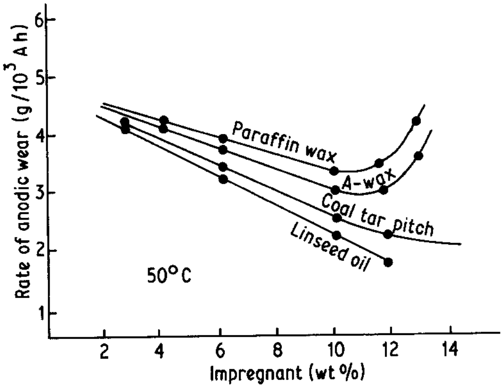

Fig. 4. Rate of wear versus weight per cent impregnant for impregnated graphite anodes in 1 M sulphuric acid solution at 50° C.

4. Discussion

The graphite anode consists of near-ideal graphite crystallites bonded together by inferior and

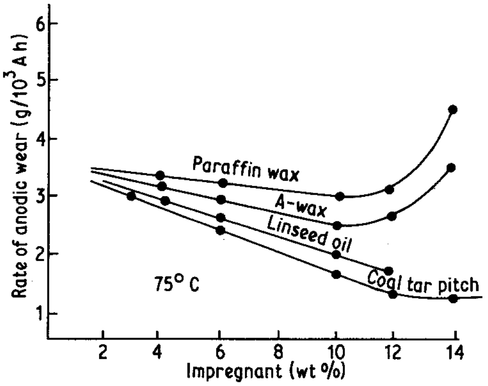

Fig. 5. Rate of wear versus weight per cent impregnant for impregnated graphite anodes in 1 M sulphuric acid solution at 75° C.

Table 2. Influence of temperature and type of impregnant on rate of wear

Bath (°C)	*Impregnant*		*Rate of wear* (g per 1000 A h)		*Ratio of outer/total wear* (%)	*Reduction in rate of wear* (%)
	Type	*Quantity* (%)	*Total*	*Outer*		
20	Paraffin wax	–	7.8	6.75	86.5	0
		4	6.7	6.68	94.0	14.1
		8	5.5	5.48	100	29.5
		10	5.0	5.0	100	35.9
		12	4.8	4.8	100	38.5
	A-wax	4	6.38	6.15	96.5	18.2
		8	5.17	5.16	100	33.7
		12	4.4	4.4	100	43.6
		14	4.7	4.7	100	39.7
	Linseed oil	4	5.78	5.69	98.5	25.9
		8	4.10	4.09	100	47.5
		10	3.2	3.2	100	59.0
	Coal tar pitch	4	6.16	5.98	97.5	21.0
		8	4.67	4.66	100	40.0
		12	3.5	3.48	100	55.1
		14	3.3	3.30	100	57.7
		16	3.25	3.248	100	58.3
50	Paraffin wax	0	4.83	4.32	89.5	0
		4	4.2	4.03	96.0	13.0
		8	3.6	3.6	100	25.4
		10	3.3	3.3	100	31.7
		12	3.42	3.41	100	29.1
	A-wax	4	4.0	3.9	97.5	17.1
		8	3.33	3.34	100	31.0
		12	2.94	2.93	100	39.1
		14	4.5	4.48	100	6.8
	Linseed oil	4	3.71	3.67	99.0	23.1
		8	2.7	2.69	100	44.0
		10	2.2	2.2	100	54.4
		12	1.7	1.7	100	64.8
	Coal tar pitch	4	3.83	3.79	99.0	20.7
		8	2.96	2.96	100	38.7
		12	2.25	2.248	100	53.4
		16	2.0	2.0	100	58.6
75	Paraffin wax	0	3.54	3.44	97.1	0
		4	3.36	3.43	97.4	5.0
		8	3.26	3.26	100	7.9
		10	3.05	3.04	100	13.8
		14	4.5	4.49	100	−27.1
	A-wax	4	3.2	3.13	98.0	9.6
		8	2.74	2.75	100	22.5
		12	2.70	2.71	100	23.7
		14	3.58	3.56	100	− 1.1
	Linseed oil	4	3.0	3.0	100	15.2
		6	2.65	2.7	100	25.1
		8	2.33	2.4	100	34.1
		10	2.0	2.05	100	43.5
	Coal tar pitch	4	2.90	2.91	100	18.0
		8	2.0	2.01	100	43.5
		12	1.46	1.47	100	58.7
		14	1.46	1.47	100	58.7

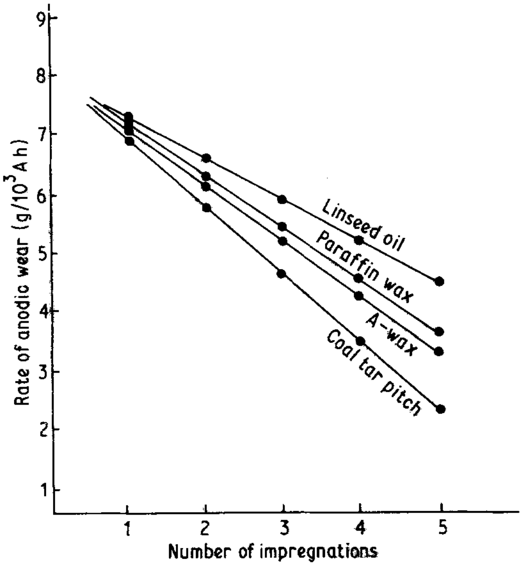

Fig. 6. Rate of wear versus number of impregnations for impregnated graphite anodes in 1 M sulphuric acid solution.

porous bridges left behind after carbonizing the electrode binder. During impregnation, the impregnant is forced into the pores thus forming a barrier between the inner surface and the electrolyte. During polarization, the graphite anodes corrode via the formation of an intermediate lamellar compound. It has been shown that [13] oxidation of graphite proceeds to the inner surfaces of the pores. With insufficient impregnation, a certain ratio of the accessible pores remains exposed to the attack of the electrolyte. If sufficient impregnation is allowed, these pores become progressively filled. This assumption finds support in the curves obtained for coal tar pitch where a constant rate of wear is approached with increasing percentage impregnation.

According to Sjodin and Wranglén [3] linseed oil and paraffin wax add oxygen with consequent volume increase. If the impregnants were solid, completely filling the pores, the pressure created by this volume increase would break the graphite material thus increasing the anodic wear. Using this assumption, they explained the occurrence of a minimum corrosion rate at an optimal content of about 10% linseed oil. It is, however, more reasonable to suggest the following model. The process of impregnation involves the flow of the impregnant into pores of different diameters. These pores are more easily accessible to impregnant with lower viscosity. In other words the pore entrance may be blocked more readily the higher the viscosity. This does not imply, however, that the inner surface of the pores has been completely covered. Thus the curves obtained for less viscous impregnant like linseed oil do not show a minimum or reveal a tendency towards a constant value of wear rate.

It may be assumed that early blocking of the pores results in an increase in current density at the uncovered areas with consequent increase in corrosion rate at these areas. Subsequently, the impregnant particles will be loosened or fall off the electrode surface. These conditions may prevail for waxes. On the other hand, coal tar pitch sticks to the surface in spite of the wear of the uncovered surface areas. The fact that the efficiency of coal tar pitch as an impregnant does not decrease with increasing bath temperature may be explained on the premise that it contains resinous components which have relatively high melting points. On the other hand the other three impregnants, having lower melting points, are squeezed out of the electrode with rise in temperature.

Multiple impregnation is effective in reducing the number of accessible pores. The impregnant, originally occupying a larger volume and blocking the entrances of the pores, undergoes charring with subsequent laying down of carbon which occupies less volume allowing for more uptake of another amount of the impregnant. The high response of the anodic wear to the number of impregnations may be correlated with the coking value of the impregnant. Coal tar pitch having the highest coking value produces the highest reduction in corrosion rate. Linseed oil, on the other hand, having a lower coking value, needs a larger number of impregnations to achieve a certain reduction in anodic wear as compared with coal tar pitch.

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