

<https://doi.org/10.3176/oil.1998.1.05>

## INVESTIGATION INTO MAKING ELECTRICALLY CONDUCTIVE FILLERS FROM OIL SHALE ELECTRODE COKE

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*The problems of calcining and grinding of electrode coke made from Estonian oil shale were studied with the view to obtain conductive fillers for preparing electrically conductive compositions.*

*Calcining of crude coke in the temperature range of 800-1000 °C with the following disintegration was found to yield electrically conductive fillers with the resistivity of  $1.8 \cdot 10^{-2}$ - $2.4 \cdot 10^{-2} \Omega \cdot \text{cm}$  and particle size of 1-4  $\mu\text{m}$ . The obtained fillers are suitable for producing antistatic conductive compositions.*

### Introduction

Presently the use of electrically conductive plastics, which can be easily manufactured, have low specific gravity and high corrosion resistance, are low-priced, etc., is widely spread in several branches of industry. Conductive plastics can be made by two methods, incl. synthesis of plastics with a special structure or making electrically conductive compositions based on polymers and electrically conductive fillers. Among the latter the most widely used are carbon black, graphite and fine dispersed powders, flakes or fibres of several metals (Ni, Cu, Al, Ag, Au) as well as carbon fibres. In addition to the named materials, conductive coke is also introduced as a filler.

In papers [1-3] conductive coating compositions for elongated conductors, in particular for automotive ignition cables, made from the ground coal-based calcined coke and organic binding materials are given. The compositions used earlier for this purpose were made from high-quality graphites to accomplish high conductivity. The negative characteristics of these materials include high cost and relatively rapid

decomposition rate due to peroxides introduced in the compositions. The electrically conductive materials based on coke are significantly cheaper, coke is resistant to corrosion by peroxides and it can be introduced in the compositions in essentially higher quantities than graphite without increasing the viscosity of the materials significantly [2]. Various resins and elastomers, including inorganic materials, as for example water glass, can be used for binding materials as required by the application.

In the work [4] inexpensive electrically conductive adhesives produced from oligomers or viscous solutions of polyvinylchloride, polyesters or acrylic resins and powdered coke with the particle size below 100  $\mu\text{m}$ , mainly 5-50  $\mu\text{m}$  are patented. The electrical resistance of these materials is in the range from 10 to  $10^3 \Omega \cdot \text{cm}$ . Some antistatic conductive resins with good mouldability have been made from powdered coke with the particle size below 100  $\mu\text{m}$  in combination with carbon black and thermoplastics [5].

It has been found [6] that the use of calcined coke to yield electrically conductive coatings, which produce heat from the traversing electrical current is superior to the use of carbon black and graphite. Such above-mentioned coatings have improved tensile strength, uniform electrical conductance and heat generating characteristics for the extensive period of use. Petroleum coke has been found to be more easily dispersible in the heating compositions, generally providing a composition much easier to apply than the equivalent coatings based on graphite or carbon black. The conductive compositions of the present invention with the resistivity of 0.4-30  $\Omega \cdot \text{cm}$  were made from the calcined powdered petroleum coke with the resistivity of 0.27  $\Omega \cdot \text{cm}$ , and polymeric latexes.

It can be seen from the above that the majority of the described patents show dispersity of the used ground coke. But at the same time there is no data available on preparing cokes with the required resistivity and dispersivity. Thus, it seems expedient herewith to present some data on the interdependence of the coke conductivity and the thermal processing conditions. In the work [7, 8], it is shown that for the given coal the resistivity of coke is highly dependent on the coking temperature. It is especially pronounced in the temperature range of 500-900  $^{\circ}\text{C}$  where the resistivity decreases up to 10 times with raising the temperature for 30-50  $^{\circ}\text{C}$ . At the coking temperature over 1000  $^{\circ}\text{C}$ , the resistivity decreases essentially slower versus the temperature growth. In the same work the resistivities of highly compacted powdered coke obtained at the temperature of 1000  $^{\circ}\text{C}$  are presented. These resistivities remain within the range of 0.012-0.003  $\Omega \cdot \text{cm}$  or 0.025-0.05  $\Omega \cdot \text{cm}$ . Similar results have been obtained in [8] where it is shown that with changing the final calcining temperature of coke in the range of 700-1000  $^{\circ}\text{C}$ , the resistivity decreases within the same limits independent from the type of coal. In [9] the data close to the given results have been obtained also for the



petroleum cokes, i.e., up to 500 °C where no significant changes occur in the coke structure and conductivity. More pronounced changes can be observed above the temperature level of 550 °C while over 1150 °C decelerating significantly. The change in the electrical properties of cokes is extremely rapid in the temperature range of 500–700 °C where the gas emission reaches its maximum. The above shows that for manufacturing electrically conductive fillers from coke, suitable calcining and powdering to the particle size below 150 µm is required while the powders with higher dispersity (5–50 µm) are preferred.

In the present paper the possibilities for manufacturing electrically conductive fillers from a local raw material, i.e. oil shale electrode coke, for making conductive compositions and the conditions for producing fine dispersed powders and their calcining were investigated. Therefore the problems of grinding electrode coke, dependence of the resistivity from calcining temperature and potentialities for the use of the obtained materials in making electrically conductive compositions were studied.

The objective of the work was to find additional implementation to local resources for producing antistatic coatings where the residues of polyvinyl chloride could be used as a polymeric binder, or electrically conductive paints on the basis of polymeric latexes, etc.

## Experiments

### Grinding

For grinding the electrode coke produced at Kohtla-Järve, the method of disintegration was studied as one of the most promising due to the high productivity and the available scientific and technical basis. A lab disintegrator DESI 11M 1E made in the production company *Desintegraator* was used. The named disintegrator had both finger and blade rotors, which allowed to use both technologies for sample disintegration. The characteristics of crude coke, i.e. coke without additional thermal treatment, and those of cokes with preliminary calcining were investigated. The influence of the repeated disintegration on the particle size and the fractional consistence was investigated and the productivity of additionally disintegrated powders in the ball mill was determined. For the disintegration method, all the grindings were carried out with the same rotation velocity of 10 200 turns/min, which is the maximum velocity of the device. Lower velocities did not give satisfactory results since the obtained powders included particles of larger diameters in significant amounts.

The oil shale electrode coke was calcined at 900 °C in the CO<sub>2</sub> atmosphere before grinding during 3.5 hours. The obtained results are given in Table 1.

Table 1. Grinding of Oil Shale Electrode Coke by the Disintegration Method

Disintegration method	Number of disintegration procedures	No. of test	Particle size, $\mu\text{m}$	Particle distribution, %		
Thermally untreated oil shale electrode coke						
Blade rotors	1	1	1	—		
			2	—		
			4	20		
			9	63		
			18	15		
			36	2		
Blade rotors	2	2	1	0		
			2	—		
			4	20		
			9	64		
			18	15		
			36	2		
Finger rotors	1	3	1	—		
			2	—		
			4	19		
			9	60		
			18	19		
	36	2				
	Finger rotors	2	4	1	—	
				2	—	
				4	22	
				9	65	
18				13		
36	—					
Oil shale electrode coke calcined at 300 °C for 3.5 h						
Finger rotors	1	1	1	22		
			2	34		
			4	29		
			9	11		
			18	4		
		36	1			
		Finger rotors	2	2	1	23
					2	47
					4	23
					9	6
					18	1
		36	—			
		Finger rotors	3	3	1	28
					2	51
					4	18
9	3					
18	—					
36	—					

## Dependence of Resistivity from the Calcining Temperature of Oil Shale Based Electrode Coke

Dependence of the resistivity of oil shale based electrode coke from the calcining temperature was studied in the temperature range of 500-1000 °C.

Previously disintegrated samples and crude coke without preliminary grinding were used. In all cases the samples were calcined in an inert medium. Powdered samples were calcined in a tube furnace under the stream of nitrogen or carbon dioxide, and crude coke in the electrical furnace ЧОА 2.54 · 1.4/II-I with the CO<sub>2</sub> medium.

*Table 2. Dependence of Powdered Coke Resistivity from the Time and Temperature of Sample Calcining (N<sub>2</sub>)*

Sample No.	Calcining temperature, °C	Calcining time, h	Resistivity, Ω · cm
1	—	—	$3.4 \cdot 10^8$
2	500	3.5	$3.4 \cdot 10^8$
3	600	3.5	$1.7 \cdot 10^4$
4	600	7.0	$3.5 \cdot 10^2$
5	700	3.5	7.24
6	700	7.0	$8.6 \cdot 10^{-1}$
7	800	3.5	$3.4 \cdot 10^{-1}$
8	800	7.0	$2.0 \cdot 10^{-1}$
9	800	14.0	$3.5 \cdot 10^{-2}$
10	900	3.5	$8.0 \cdot 10^{-2}$
11	900	7.0	$4.2 \cdot 10^{-2}$
12	1000	1.0	$2.4 \cdot 10^{-2}$
13	1000	1.0	$2.4 \cdot 10^{-2}$
14	1000	1.0	$2.4 \cdot 10^{-2}$
15	1000	3.5	$1.8 \cdot 10^{-2}$
16	1000	3.5	$2.4 \cdot 10^{-2}$
17	1100	1.0	$1.8 \cdot 10^{-2}$

The resistivity of the obtained powders was determined on compacted samples fixed between two contacts made from stainless steel. The measuring was organized in such a way that the voltage and current were measured while the resistivity was calculated from the results. Since for powders the resistivity is highly dependent on the compacting pressure, it was determined experimentally that beginning from the pressure  $1.96 \cdot 10^7$  N/m<sup>2</sup> the resistivity would not continue to decrease. Based on the above observations, all the studied samples were compacted at the named pressure. Table 2 gives the data on the variation of the calcining electrode coke resistivity relative to the temperature and time of heating the powdered samples in the nitrogen flow.

Application of carbon dioxide as an inert medium instead of nitrogen had no impact on the value of the resistivity. At calcining crude coke, the big lumps were heated together with powdered samples for getting the



comparable data in the  $\text{CO}_2$  medium at the temperature of  $880^\circ\text{C}$  during 11 hours. The resistivity of powders made from crude coke remained within the range of  $1.8\text{-}2.4 \cdot 10^{-2} \Omega \cdot \text{cm}$  and that of the powder samples heated under similar conditions was  $2.4 \cdot 10^{-2} \Omega \cdot \text{cm}$ .

**Table 3. Dependence of Coke Weight Loss from the Time and Temperature of Sample Calcining**

Sample No.	Calcining		Weight loss, %		Resistivity, $\Omega \cdot \text{cm}$
	$t$ , $^\circ\text{C}$	Time, h	$t$ raising $100^\circ\text{C}$	Total	
1A	500	3.5		4.9	$3.4 \cdot 10^8$
1B	500	3.5		8.9	$3.4 \cdot 10^8$
2A	600	3.5		13.8	$1.7 \cdot 10^4$
2B	600	3.5	6.1	15.0	$5.5 \cdot 10^3$
3A	700	3.5		21.7	7.2
3B	700	3.5	7.3	22.3	$5.1 \cdot 10^{-1}$
4A	800	3.5		22.6	$3.4 \cdot 10^{-1}$
4B	800	3.5	5.2	27.3	$8.3 \cdot 10^{-2}$
5A	800	7.0		34.3	$2.0 \cdot 10^{-1}$
6A	800	14.0		37.7	$3.5 \cdot 10^{-2}$
7A	880	11.0		40.4	$2.4 \cdot 10^{-2}$
8A	900	3.5		26.2	$8.0 \cdot 10^{-2}$
8B	900	3.5	5.3	32.4	$3.6 \cdot 10^{-2}$
9A	900	7.0		30.8	$4.2 \cdot 10^{-2}$
10A	1000	3.5		23.9	$1.8 \cdot 10^{-2}$
10B	1000	3.5	5.3	38.1	$2.4 \cdot 10^{-2}$
11A	1100	1.0		23.0	$1.8 \cdot 10^{-2}$

**Table 4. Dependence of the Composition Resistivity from the Type and Content of the Conductive Filler**

Sample No.	Conductive filler		Resistivity range for parallel samples, $\Omega \cdot \text{cm}$
	Name	Amount, %	
1	Carbon black	22	$>10^6$
2	Carbon black	31	$1.8 \cdot 10^4\text{-}2.5 \cdot 10^3$
3	Carbon black	40	$(3\text{-}6) \cdot 10^2$
4	Graphite	31	$>10^6$
5	Graphite	47	$1.2 \cdot 10^4\text{-}1.6 \cdot 10^3$
6	Coke	31	$>10^6$
7	Coke	47	$(1.5\text{-}2.2) \cdot 10^3$

The emission regularities of flying products were studied during the heating procedures at different temperatures for the determination of the interrelation between the resistivity and the thermal treatment. Two series of tests were carried out. In the first case, the powdered samples (A-series) were heated during different time intervals at the defined temperature and the weight loss was determined. In the second case

(B-series), all the test were carried out with the same sample by heating the sample at each temperature level under consideration for 3.5 hours with the weight loss established after that. For all tests, the resistivity of samples was determined. The data on the results is given in Table 3.

### **Possible Application of the Conductive Fillers Made from Electrode Coke**

The suitability of electrically conductive fillers from oil shale electrode coke for fabricating conductive compositions was tested by using the material obtained from calcining crude oil shale electrode coke in the  $\text{CO}_2$  medium at the temperature of  $880^\circ\text{C}$  for 11 hours and the following disintegration

The obtained powder had the resistivity of  $2.4 \cdot 10^{-2} \Omega \cdot \text{cm}$  and the particle size of 1-36  $\mu\text{m}$ . The data on the powder is given in Table 1.

As a comparative material, carbon black with the resistivity of  $2 \cdot 10^{-2} \Omega \cdot \text{cm}$  and high quality graphite with the particle size below 62  $\mu\text{m}$  were used. They were heated for the removal of absorbed additives at the temperature of  $250^\circ\text{C}$  for 8 hours before fabricating compositions.

As a binding material, the Si-organic rubber СИЭЛ(SIEL)-159-274 and the polyvinyl chloride powder made from industrial waste were used.

The samples based on Si-organic materials in the amount of  $\sim 5\text{ g}$  were prepared by mixing the ingredients (filler, rubber, catalyst of vulcanization) by hand. The films of compositions with the thickness of 1-1.5 mm were made between two teflon plates and were then vulcanized at the temperature of  $150^\circ\text{C}$  for 30 hours. From these films 10 mm straps were cut and their resistivity was measured. The obtained results are given in Table 4.

The point scattering in the values of resistivity of parallel samples is results from mixing the compositions by hand, which does not provide completely reproductive results. The difference in the range of the values of resistivity is due to the dissipation of the results of parallel samples since the mixing of compositions by hand does not provide reproductive results. For carbon black, the maximum yield of the filler reaches 40%. In case of higher content, the samples cannot be mixed any more. Coke gave the samples of the lowest viscosity and therefore with high mixing capacity, which can be seen from the relatively stable value of the resistivity of different samples. For the use of polyvinyl chloride as a binding material, the resistivity of coke based compositions remained practically of the same order as the above given results, i.e.,  $10^3 \Omega \cdot \text{cm}$ . But for the carbon black and graphite, the results were much better, i.e., of the value of  $10 \Omega \cdot \text{cm}$ . The given results are of approximate value since for the lack of necessary mixing devices making polyvinyl chloride based compositions is a rather complicated task.



## Discussion

The data from Table 1 shows the applicability of the disintegration method for producing fine dispersed powders from the oil shale electrode coke. For all the investigated cases the maximum particle diameter obtained was 30  $\mu\text{m}$ . Thus the particle size of the prepared powders was somewhat smaller than that for the conductive fillers made from the cokes described in the literature. The rotor-type and repeated disintegration had no noteworthy effect on the obtained results. But the thermal treatment (880  $^{\circ}\text{C}$  for 11 hours) preceding the disintegration had essential influence on the dispersity of coke powders. With the disintegration of crude coke, a powder with the prevailing particle size of 4–18  $\mu\text{m}$  was formed while the disintegration of previously calcined electrode coke gave the particle size of 1–4  $\mu\text{m}$  for a fraction. In the first case 80 % of particles had the diameter of 9–36  $\mu\text{m}$  while for the second case their share was only 17 %. Thus the preliminary thermal treatment of the coke before disintegration provides for making more dispersed powders. With the following grinding of the sample in the ball mill the content of larger particles decreases or they disappear relative to the grinding time and the content of 1–2  $\mu\text{m}$  particles in the powder increases.

Investigation of the interrelation between the resistivity of electrode coke powders and their thermal treatment showed (Table 2) that the resistivity of the coke remained unchanged when the sample was heated at the temperature below 500  $^{\circ}\text{C}$ . In the temperature range of 500–700  $^{\circ}\text{C}$  the maximum decrease of resistivity, i.e.  $10^8$  times, took place. During the further temperature raise the decrease of the resistivity was significantly lower. Furthermore, it can be seen from the given data that with the prolongation of the time of thermal treatment the value of the resistivity decreases also, i.e., the more rapid the decrease is, the lower the temperature drops. The twofold extension of the time of thermal treatment decreases the resistivity for  $\sim 50$  times at the temperature of 600  $^{\circ}\text{C}$ , at 700  $^{\circ}\text{C}$  the decrease reaches 8 times and at 900  $^{\circ}\text{C}$  it decreases only twice. At the temperature of 1000  $^{\circ}\text{C}$  the prolongation of heating time from one hour to 3.5 hours shows no significant decrease in the resistivity. Raising the temperature further up to 1100  $^{\circ}\text{C}$  gives also no significant lowering of the resistivity and it remains within the limits of  $(1.8\text{--}2.4) \cdot 10^{-2} \Omega \cdot \text{cm}$ . This result remains within the same limits as the resistivity of coal coke powders  $(1.2 \cdot 10^{-2}\text{--}5 \cdot 10^{-2} \Omega \cdot \text{cm})$  [7] and is an order lower than that of the electrically conductive filler made from oil coke  $(2.7 \cdot 10^{-1} \Omega \cdot \text{cm})$  by preparing conductive compositions in [6].

The study of the emission regularities of volatile products at different temperature regimes (Table 3) shows that by calcining crude oil shale coke, the maximum emission of gases takes place in the same



temperature range where the change of the resistivity is the highest, i.e., up to the temperature of 700 °C. For the A-series of samples 21.7 % of flying substances emit within 3.5 hours. With raising the temperature to 1000 °C, only ~2 % of weight loss is added to this value at heating during 3.5 hours. It can be seen further that the prolongation of heating time increases the weight loss significantly, evidently probably due to two reasons. First, the prolonged time of thermal treatment allows the process in the examined material to be completed or almost completed. Second, both nitrogen and carbon dioxide contain some oxygen, which reacts with the carbon resulting in the emission of the latter as CO<sub>2</sub>.

The longer the heating time, the higher the carbon loss. For the given reasons, the weight loss of A-series samples is lower than the total weight loss of the B-series samples since in addition to the time of calcining, the time of elevating the temperature to the required value is combined with the following cooling time here. This is why the resistivity of the B-series of samples after thermal treatment at the given temperature remains essentially lower than that of the A-series of samples. Proceeding from the above, it seems more suitable to calcine crude coke at a higher temperature for a shorter period. The investigation of the possible use of oil shale electrode coke based conductive fillers for making conductive Si-organic compositions showed that there is no significant difference between the fillers from graphite and those from oil shale electrode coke since for both cases the resistivity of compositions remains of the order  $10^{-3} \Omega \cdot \text{cm}$  while with the use of the coke the composition can be better treated due to its lower viscosity.

Better results were obtained with the use of carbon black ( $10^2 \Omega \cdot \text{cm}$ ) when its maximum possible content in the composition was used. At the same time, carbon black based compositions were very viscous and difficult to treat. When using polyvinyl chloride as a binding material, the resistivity of compositions was the same as that of the Si-organic materials. The use of carbon black and graphite gave better results for the given binding material.

## Acknowledgments

The research was financially supported by Estonian Science Foundation.

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*Presented by L. Mölder*

Received September 19, 1997