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(71) Applicant: **THE STANDARD OIL COMPANY**
Midland Building
Cleveland, Ohio 44115(US)

(72) Inventor: **Kiikka, Oliver Adneil**
36222 Skytop Lane
Willoughby Ohio 44094(US)

(72) Inventor: **Connors, Keith Allan**
206 Simmons Drive
Moundsville West Virginia 26041(US)

(74) Representative: **Smith, Sydney et al,**
Elkington and Fife High Holborn House 52/54 High
Holborn
London WC1V 6SH(GB)

(54) **Reduction of reactivity in coke.**

(57) Carbon dioxide and air reactivity reactions which occur during carbon electrode use, are reduced by treating the coke used to make the electrode after calcination with water containing a monomeric, dimeric or polymeric-phosphoric acid, or a salt thereof. A representative acid is orthophosphoric acid.

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Title

Reduction of Reactivity in Coke

The present invention relates to reducing the reactivity of coke and in particular its carboxy reactivity and air reactivity which are important during carbon electrode use.

5 As noted in U.S. Patent No. 4,130,475, coke formed from petroleum refinery streams is classified as No. 1 or premium coke, and No. 2 or regular coke. Premium coke differs from regular coke by its pre-
10 dominant metallic, crystalline appearance and a low linear coefficient of thermal expansion (CTE).

Both types of coke are used for the manufacture of carbon electrodes utilized in industry. The steel industry uses electrodes formed from premium coke in electric arc furnaces, while the aluminium
15 industry uses electrodes formed from regular coke to produce aluminium. The description of such use in making aluminium can be found in Kirk-Othmer
Encyclopedia of Chemical Technology Vol. 1, page 941.

Prior to the formation of electrodes, the
20 refinery petroleum coke must first be calcined. Calcination usually occurs with temperatures in excess of 2200°F, (1204°C), preferably above 2500°F (1371°C). The calcination densifies the coke and removes volatile matter while changing the carbon to hydrogen ratio.

25 The coke which leaves the calciner at these high temperatures must then be cooled. This is typically accomplished in a cooler wherein water is sprayed onto the coke. The water by evaporation cools the coke to a suitable temperature. This
30 calcined, cooled coke is then formed into electrodes.

As noted in the Kirk-Othmer reference, aluminium is formed by the electrolysis of alumina wherein the oxygen from the alumina combines with the carbon of the electrode to form carbon dioxide. A second and
5 unwanted reaction occurs when the carbon dioxide again reacts with the carbon to form carbon monoxide. While 0.45 lbs. per lb. of aluminium is utilized for the electrolysis, 0.05 lbs. of carbon per lb. of aluminium is lost in forming carbon monoxide. The ability of
10 a carbon electrode to react with CO_2 to form carbon monoxide is known as the carboxy reactivity.

In the steel industry, electrodes are used in arc furnaces for melting of steel. A similar unwanted reaction occurs with air reacting with the carbon to
15 form carbon oxides. Typically, 15-25% of the carbon is lost to this air reactivity reaction.

U.S. Patent No. 3,320,150 notes that high reactivity can sometimes be due to the type of binder material or binder coke that is used and thus suggests a decrease
20 in reactivity by utilizing a fine coke with a reactivity lower than the binder coke. U.S. Patent No. 3,454,363 discloses the removal of metal contaminants from coke to lower reactivity. It is noted that the presence of cations is detrimental to some of the
25 potential applications of coke, and thus the coke is contacted with a cation exchange resin to remove cations and thus lower reactivity.

It has now been found that if the water used to quench calcined coke is treated with phosphoric
30 acid, a lower reactivity and thus a better product can be obtained.

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The invention therefore provides a process for reducing the reactivity of calcined coke by the steps of:

- a) calcining the coke to densify and remove
5 volatiles therefrom; and
- b) cooling said calcined coke by contacting said coke with water treated with a monomeric, dimeric, or polyphosphoric acid or a salt of such an acid or one or more such acids or salts thereof.

10 The calcining of coke is known to those in the art and is typically accomplished in a rotary calciner. Calcining temperatures are usually in excess of 2200°F (1204°C), with coke exiting the calcining at temperatures as high as 2700°C (1482°C).

15 The coke is then cooled in a cooler as described previously, by directly contacting the coke with water. It is desired to cool the coke to a temperature of around 300°F (149°C), and thus air cooling is uneconomical. Typically, it takes approximately 1 lb.
20 of water per lb. of coke during this cooling process. Normally well water has been utilized as a source for this cooling stage.

The treatment of water is also well known in the art. A good description of the type of treatment
25 available can be found in Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 22, page 73 and Power Magazine, June 1973, page S-1.

As described in the Power article, water normally contains a variety of dissolved compounds, with each
30 compound breaking into its respective charged part or "ion" when dissolved. Positively charged ions are called cations while the negatively charged ions are called anions.

The treatment of the water used to cool
35 calcined coke with an

ion exchange resin to remove cations which have been shown to effect reactivity would involve great expense because of the large quantities of water involved.

The water cannot be recycled due to evaporation. It has been discovered that the addition of phosphoric acids such as monomeric, dimeric or polyphosphoric acid and salts thereof to the cooling water in parts per million amounts have a dramatic effect on the reactivity of the coke.

Some species of phosphates have been used in water treatment systems to prevent corrosion and deposits in distribution lines. These have included polyphosphates such as sodium hexametaphosphate or sodium tripolyphosphate in less than stoichiometric amounts. The addition of polyphosphates inhibits calcium carbonate deposition by sequestration. However, due to the fact that evaporation occurs when utilizing water as a cooling agent to calcined coke, the use of these polyphosphates would not be expected to have any effect on the reactivity of the coke.

Surprisingly, it has been found that the above noted phosphoric acids, preferably orthophosphoric acid, and salts thereof have a dramatic effect on reducing the reactivity of the calcined coke when used in amounts of 1,000 ppm or less.

For purposes of illustration, the invention will now be described with respect to the use of orthophosphoric acid.

The amount of acid to be added to the water used for cooling depends upon the type of water being utilized and the degree of reduction in reactivity preferred. For most waters, including well water, it has been found that amounts between 5-1,000 ppm

are sufficient. While reactivity does decrease in the use of amounts and the 20-80 ppm range, a preferred range may be stated between 100-600 ppm.

The orthophosphoric acid may be injected into the water stream at any point prior to the water contacting the hot calcined coke. Injection systems for addition of small amounts of additives into aqueous mediums is well known in the art and need not be described in detail.

The following examples show the effect of using cooling water treated with orthophosphoric acid and its effect on CO₂ Reactivity (RCO₂). This value is determined by sampling the coke to be tested and drying it at 120°C to a constant weight. This weight was recorded as the initial sample weight, or "WI". The sample was then inserted into a furnace operating at 1,000°C. CO₂ was flowed over the sample at approximately 50 normal litres per hours for two hours. The sample was then cooled in a desiccator, with the final weight being recorded as "WF". CO₂ Reactivity was then calculated as follows:

$$\text{CO}_2 \text{ Reactivity} = \frac{\text{WI} - \text{WF}}{\text{WI}} \times 100$$

Comparative Example A

Calcined coke at a temperature of approximately 2600°F (1426°C) was cooled by spraying untreated water onto the coke. The CO₂ reactivity is noted in Table I.

Examples 1-2

To show the effect of orthophosphoric acid addition, orthophosphoric acid was first diluted with water prior to injection. A metering pump was

then used to inject the mixture into cooling water lines going to the spray heads for cooling the calcined coke. Examples 1 and 2 show the effects of the addition of low quantities of phosphoric acid to the CO₂ reactivity values.

Table I
Effect of Low ppm Addition of
H₃PO₄ to Cooling Water

<u>Example</u>	<u>H₃PO₄ Conc. PPM</u>	<u>% RCO₂</u>
Comp. Ex. A	0	21.7
1	30	17.1
2	49	15.7

In the same manner as the above examples, Table II below shows the effect of higher rates of addition of phosphoric acid to the cooling water.

Table II
Effect of High ppm Addition of
H₃PO₄ to Cooling Water

<u>Example</u>	<u>H₃PO₄ Conc. PPM</u>	<u>% RCO₂</u>
Comp. Ex. B	0	23.6
3	100 ppm	14.5
4	200 ppm	11.0
5	400 ppm	5.6

As can be seen in the above examples, substantial reduction in the CO₂ reactivity values can be obtained when utilizing orthophosphoric acid in the water used to cool the calcined coke.

Claims:

1. A process for producing a calcined coke of reduced reactivity wherein the calcined coke is cooled after calcination to densify it and remove volatiles by contacting it with water treated with a monomeric, dimeric, or polyphosphoric acid or a salt of such acid.
2. A process as claimed in claim 1 characterised in that the water is treated with a monomeric phosphoric acid.
3. A process as claimed in claim 1 characterised in that the water is treated with a dimeric phosphoric acid.
4. A process as claimed in claim 1 characterised in that the water is treated with a polyphosphoric acid.
5. A process as claimed in claim 2 characterised in that the water is treated with orthophosphoric acid.
6. A process as claimed in claim 5 characterised in that the amount of orthophosphoric acid added to the water is between 5-1000 ppm.
7. A process as claimed in claim 6 characterised in that the amount of orthophosphoric acid added to the water is between 100-600 ppm.
8. A process as claimed in any of claims 1 to 7 characterised in that the coke has been calcined at a temperature greater than 2200°F (1204°C).