DRIYING OIL IMPREGNATION OF CARBON ELECTRODES

CARBON ELECTRODE

GRAPHTICIZED CARBON ELECTRODE

PREHEAT ELECTRODE

VACUUM TO EVACUATE PORES

IMPREGNATE WITH DRYING OIL USING VACUUM AND AIR PRESSURE

RELEASE PRESSURE AND DRAIN OFF EXCESS OIL

CONTACT ELECTRODE WITH STEAM AT A PRESSURE OF AT LEAST 300 PSI

RELEASE HIGH PRESSURE STEAM QUICKLY

VACUUM TO REMOVE THE EXCESS OIL BLOWN OUT OF ELECTRODE PORES BY THE "STEAM BLOW"

CONTACT ELECTRODE WITH LOW PRESSURE STEAM TO CLEAN ITS SURFACE

COOL ELECTRODE

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The invention relates to improvements in the production of carbon electrodes employed in electrolytic cells. More particularly, this invention relates to a new and useful treatment of polymerizable oil-containing carbon electrodes such as are employed in chlorine-alkali type electrolytic cells, particularly of the diaphragm type.

It is known that when carbon electrodes, such as graphite anodes used in electrolytic cells, for the production of caustic and chlorine, are placed in operation without any treatment, they have a relatively short cell life. It is also known that if such graphite anodes are first impregnated with a drying oil such as linseed oil, their cell life is approximately doubled. However, experience has shown that under normal impregnation conditions of a vacuum-pressure cycle, an excessive amount of oil remains in the anode pores and the excess oil exudes to the surface of the anode when it is connected in or "leaded" into the cell and during operation of the cell.

The oil exudation occurring at the joints between the lead and the graphite forms an undesirable electrical barrier, giving rise to increased resistance and a corresponding power loss.

Excessive oil within the anode also gives rise to oil exudation during cell operation. This exuded oil, and/or chlorinated oil products thereof, tend to mechanically plug the porous diaphragms employed in the cells between the anode and the cathode. Chemical plugging of the diaphragm also occurs as a result of the liberation of an excessive amount of HCl, a reaction product of the drying oil and chlorine liberated at the anode. This HCl reacts with the asbestos of the diaphragm and forms silicic acid which is gelatinous in nature and which therefore effectively plugs the diaphragm. Such plugging of the porous diaphragm restricts the flow of electrolyte and requires the cell to be shut down and the diaphragm to be cleaned or changed, resulting in a loss in production and increased cost of operation.

While details vary somewhat in commercial production of carbon anodes, generally, finely-divided coke is mixed with the desired proportions of a binder, usually a coal tar pitch. This mixing generally is carried out at an elevated temperature sufficient to liquefy the binder. The resultant mixture is then extruded and the thus-formed structure baked, typically to a temperature of about 1800°F., to remove volatile matter. At times it may be desirable to further treat the baked anode with pitch and rebake it when it is desired to further improve the anode density and strength.

Anodes produced in the foregoing manner may then advantageously be impregnated with a drying oil in accordance with this invention.

Superior results are obtained in most instances, however, when prior to impregnation with a drying oil the anode is graphitized, i.e., the carbon crystal structure is converted to the graphitic crystal structure by heating said baked anode to a temperature in the range from about 4150° to 5000° F. In other words the carbon electrodes treated in accordance with this invention may be either baked or graphitized.

In the practice of this invention excellent results may be obtained with tung oil, perilla oil, fish oil, safflower oil, soybean oil, oitica oil, or dehydrated castor oil in addition to the presently preferred linseed oil. Other oils which in many applications may be employed in lieu of or in admixture with the foregoing oils, either wholly or in part, are coconut oil, palm kernel oil, babassu oil, murumuru oil, palm oil, rape seed oil, mustard seed oil, olive oil, peanut oil, sesame oil, corn oil, cottonseed oil, soybean oil, sunflower oil, walnut oil, whale oil, menhaden oil, sardine oil and herring oil.

In addition to the previously mentioned disadvantages inherent in prior art methods from leaving an excessive amount of oil in and at the surface of the anode after impregnation, prior art impregnation procedures also fail to completely coat the available internal pore surfaces with oil. In effect then, prior art methods generally result on the one hand in excess oil impregnant left in or on parts of the anode, leading to deleterious results, and on the other hand, also give an insufficient coating of much of the available internal pore surfaces. This lack of coating or insufficient coating may be just as harmful as too much coating.

It is, therefore, an object of this invention to uniformly and substantially completely coat the pores of carbon electrodes and particularly the internal pore surfaces with drying oils and at the same time overcome the disadvantages resulting from excess residual impregnant.

It is an additional object of this invention to provide a procedure whereby the amount of drying oil retained in the pores of the electrode impregnated with said oil is easily and by a readily controlled procedure reduced to a desirable amount.

It is yet another object of the present invention to accomplish the foregoing objectives and at the same time to produce impregnated electrodes which have good "leading in" qualities, i.e., electrodes which do not cause undesirable electrical barriers at the joints between the lead in the cell and the graphite.

Additional objections will also become apparent from a study of the accompanying drawings and from a reading of the following detailed description of the invention.

It has now been found that by employing a high-pressure "steam-blow" technique following drying oil impregnation of carbon electrodes, the excess absorbed drying oil may conveniently be expelled and the final percentage of residual drying oil kept within acceptable limits. Generally acceptable limits for drying oil content are from about 6% to about 10%, based upon the weight of the carbon electrode, throughout an electrode apparent density range of from about 1.45 to about 1.70. Better control of oil content can be maintained when the apparent density of the electrode is between about 1.50 and about 1.60.

It has additionally been found that such high pressure "steam-blow" technique, besides facilitating the expulsion of excess drying oil also makes possible a uniform and substantially complete coating of the internal pore surfaces of the electrode.

Such a high pressure "steam-blow" technique comprises applying high pressure (in the region of 300 p.s.i. or above) steam to the fully impregnated electrode and then suddenly or quickly releasing this pressure, whereby the excess drying oil is driven out of the electrode, thereby causing a uniform but not excessive coating of oil of all the internal pore surfaces of the carbon structure.

In the preferred practice of this invention two or more such high pressure "steam-blow"s are employed, although a single such blow is sufficient in many cases.

By thus controlling the amount and state of dispersion of the oil remaining in the pores, and keeping it at the proper level, the plugging of the porous diaphragm between the anode and cathode during the operation of the cell is substantially reduced or eliminated, while the oil remaining in the pores is sufficient to protect the carbon
from deterioration, particularly by oxidation, during the operation of the cell.

The following detailed procedure of an impregnation-expulsion cycle will further illustrate the teachings of this invention.

Example 1

A graphite anode having an apparent density of 1.60 grams per cubic centimeter was placed in a suitably equipped autoclave and was preheated with 95 p.s.i. steam for 15 minutes. The steam was then released and the autoclave evacuated. Linseed oil, preheated to about 100° C. and to which about 10% by weight cobalt napthenate drier had been added, was drawn into the autoclave while maintaining the vacuum. After sufficient oil to cover the anode had been drawn into the autoclave, air pressure at 95 p.s.i. was applied to facilitate impregnation. After releasing the pressure, the excess oil was drained off and steam applied to the anode until a pressure of 400 p.s.i. was attained, at which time the high pressure steam was suddenly or quickly released by means of a quick action valve. A vacuum was again applied to pull to the surface of the anode the excess oil blown out of the pores by the steam blow. Approximately 5 p.s.i. steam was then applied to clean the surface of the anode after which the anode was removed from the autoclave and cooled.

The foregoing procedure, utilizing the novel and important high pressure "steam-blow" technique, effects considerable reduction in anode oil content compared to a similar procedure but which does not employ this step, and also makes possible the achievement of the aforedescribed objects of the present invention, such as uniform and more complete coating of the available internal pore surfaces.

Tests made of several electrodes show that original oil contents, after impregnation but before a "steam-blow," range from about 12% to about 17% through an anode density range of 1.45–1.70. With a single 400 p.s.i. "steam-blow" the oil pickup can be brought within the acceptable 6%–10% specifications. A minimum steam pressure employed in this "steam-blow" technique should be approximately 300 p.s.i. Pressures below this do not bring about the desired reduction in oil content, nor are the internal pore surfaces as completely and as uniformly coated with oil.

As previously stated, it is also important that the carbon electrodes used in electrolytic cells be efficiently "leaded into" such cells without excessive oil exudation, the latter causing an undesirable electrical barrier at the joint between the lead of the cell and the graphitic. In order to determine whether variously treated impregnated electrodes would "lead test" successfully, the electrodes were tested under conditions simulating the practices employed by the chlorine-caustic industry in making the electrical connections between the electrode and the current leads. Under such test conditions impregnated carbon anodes produced in accordance with this invention evidenced no "bleeding" of oil as frequently experienced in testing similar anodes impregnated by conventional methods.

The results and findings of this invention should be noted for their great contrast with results obtained with electrodes which are subjected to "steam-blow" at 100 p.s.i. The performance levels achieved and results obtained by a single high pressure "steam-blow" as described in this invention are not attainable by a plurality or even an infinite number of "steam-blow" at 100 p.s.i. To exemplify this somewhat, several electrodes were subjected to three successive "steam-blow" at 100 p.s.i. and after such treatment only 10% gave "good" lead tests even after six weeks aging. Also, the residual oil level of electrodes of corresponding apparent density was higher after three such "steam-blow" at 100 p.s.i. than that obtained after one "steam-blow" at 400 p.s.i. In addition such electrodes did not possess the uniform and complete internal available pore coverage as did those subjected to the 400 p.s.i. "steam-blow."

In addition to and/or as a result of all of the foregoing advantages, it has been also found that the cell life of electrodes treated in accordance with the teachings of this invention has been increased to about 365 days from a cell life of about 250 days when treated with three "steam-blow" at 100 p.s.i.

It is to be understood that the invention is not limited to the specific example which has been offered merely for illustrative purposes and that modifications may be made within the scope of the appended claims without departing from the spirit of the invention.

What is claimed is:

1. In the method of treating a porous carbon electrode including the step of impregnating said electrode with a drying oil, the improvement which comprises subjecting said impregnated electrode at least once to steam at a pressure of at least 300 p.s.i. and then quickly releasing the pressure.
2. The method of claim 1 wherein the impregnated electrode is twice subjected to the treatment of high pressure steam followed by quick pressure release.
3. The method of claim 1 wherein the steam pressure employed is approximately 400 p.s.i.
4. The method of claim 2 wherein the steam pressure employed is approximately 400 p.s.i.

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