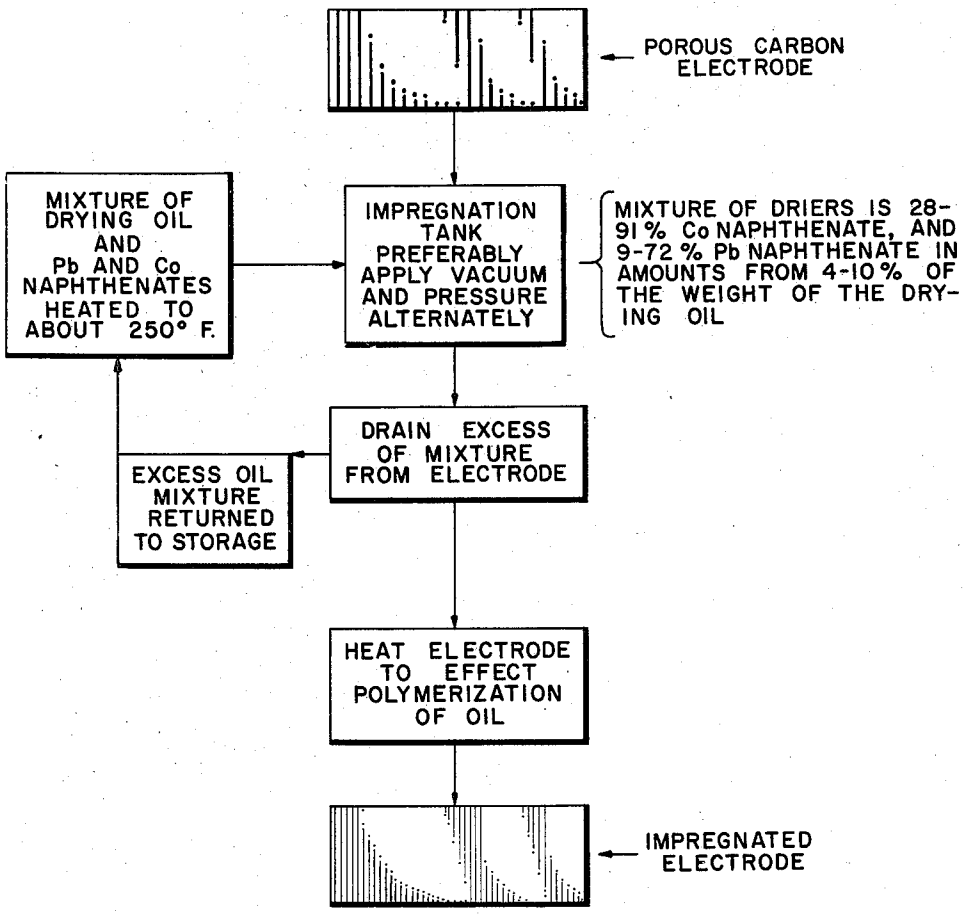
April 7, 1959 C. C. HARDMAN 2,881,100

METHOD OF IMPREGNATING A CARBON ELECTRODE WITH A DRYING OIL

Filed June 21, 1955



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United States Patent Office 2,881,100 Patented Apr. 7, 1959

2,881,100

METHOD OF IMPREGNATING A CARBON ELECTRODE WITH A DRYING OIL

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Application June 21, 1955, Serial No. 517,087

5 Claims. (Cl. 117—228)

This invention relates to improvements in electrolytic cells, and more particularly is concerned with the treatment of polymerizable oil-containing carbon electrodes for use in chlorine-alkali type electrolytic cells.

Various methods have heretofore been proposed to increase the durability and useful life of carbon electrodes in electrolytic cells. Typical of such a prior suggestion is the impregnation of a carbon electrode with a drying oil, which oil then is allowed to dry or harden in situ. In some instances, such treatment indeed is advantageous in providing a more durable electrolyte-resistant electrode. Occasionally, however, such treatment has led to difficulties in the operation of an electrolytic cell when a thus-treated electrode is first placed in use. Since the drying oil in the electrode dries or hardens rather slowly and non-uniformly, far too frequently the oil is only partially hardened or dried when the electrode is placed in service. As a result, there occurs a leaching out of the partially-cured oil and, in the case of a chlorine-alkali cell employing such an electrode as an anode, a subsequent chlorination of the oil. While this chlorination not only reduces the chlorine output of the cell and introduces undesired by-products, an additional problem is involved, since the finely-divided chlorinated oil is deposited over the cell diaphragm, thus rapidly reducing the fluid flow therethrough and generally completely plugging the diaphragm in a short time. A further inherent problem in such chlorination is the formation of by-product HCl in the anolyte, which HCl, of course, undesirably reduces the pH of the anolyte.

Prior workers in the art have sought a method to overcome these difficulties and various treatments have been proposed to eliminate or minimize these problems. Illustrative of prior suggestions and practice to improve the operating characteristics of impregnated carbon electrodes is the storage of freshly-impregnated anodes for a considerable period of time to allow gradual hardening and solidification of the oil within the anode pores, or the use of a special conditioning electrolytic cell in which the unpolymerized oil is leached from the electrode prior to use in a commercial cell. However, so far as is known, up to the present time no completely satisfactory solution to the problem had been discovered.

It is, therefore, a principal object of this invention to avoid the difficulties heretofore encountered in the operation of electrolytic cells and to provide a new and improved electrode treatment.

A further object of this invention is the provision of new and improved carbon electrodes for use in electrolytic cells.

A still further object of the invention is to provide new and improved carbon electrodes impregnated with a polymerizable oil, which electrodes do not interfere with the normal operation of an electrolytic cell.

In accordance with the present invention, a carbon electrode is contacted with a polymerizable oil and thereafter treated to effect polymerization at a greatly accelerated rate, in a novel manner. More particularly, the

present invention comprises treating a carbon electrode by contacting it with a polymerizable oil and then effecting substantially complete polymerization to preclude subsequent exudation of oil from said electrode upon its initial use in an electrolytic cell.

In accordance with this invention, polymerization of the drying oil is accomplished by combining the oil with a synergistic mixture of driers, hereinafter described. It will be appreciated that it now is possible to impregnate a carbon electrode with a polymerizable oil, with or without such prior treatment as a pitch-impregnation and/or graphitizing, and in a very short time to convert the polymerizable oil to a substantially completely polymerized substance within the carbon pores, thereby to preclude leaching of the oil from the anode upon initial use in a chlorine-alkali electrolytic cell.

Up to this time it has been known to use driers such as various cobalt compounds to accelerate the curing of various oils, especially in paints. However, the present invention is based upon the discovery that by combining two distinctly different types of driers, a novel and synergistic result is obtained. More particularly, it has been found that by combining a so-called "through" drier with a so-called "surface" drier, the polymerization of oil within a carbon electrode can be substantially completed within a relatively short time. This, of course, is in marked contrast to the extended periods of time heretofore required for anything approaching a complete polymerization of oil contained in carbon electrodes.

The expression "through drier," as used throughout the specification and claims, is intended to mean a substance which promotes substantially uniform hardening of a polymerizable oil throughout the oil thickness. Illustrative of such compounds are lead compounds, e.g., the presently preferred being lead naphthenate. Similarly, the expression "surface" drier is intended to mean a substance which produces a pronounced drying effect at the surface of a polymerizable material containing such a drier. Illustrative of such driers are various copper and cobalt compounds, for example, cobalt naphthenate which is now preferred.

In the practice of this invention, use is made of a synergistic mixture of a surface drier and a through dryer in order to obtain a substantially complete polymerization of oil within a carbon electrode without the difficulties heretofore encountered. At present, it is preferred to employ a mixture of a cobalt compound and a lead compound as the respective surface drier and through drier.

It is also now preferred to employ a major proportion of a surface drier and a minor proportion of a through drier. Superior results are obtained when these proportions are approximately 10:1 by weight, that is, 10 parts by weight of a surface drier, e.g., a cobalt compound to 1 part by weight of a through drier, e.g., a lead compound. Illustrative of a preferred embodiment of the invention is a mixture of 10 parts by weight of cobalt naphthenate with 1 part by weight of lead naphthenate. Such a synergistic mixture can be employed in lieu of, or in admixture with, prior catalysts used with polymerizable oil compositions.

It is also a feature of this invention to employ in the impregnation of carbon electrodes a polymerizable oil, preferably linseed oil, which has been treated or modified with fumaric acid to improve its polymerization properties and/or to render it more highly viscous.

In order that those skilled in the art may more completely understand this invention and its practice, the following specific examples are offered.

EXAMPLE I

A carbon electrode is impregnated with a mixture of

ten parts of raw linseed oil and one part of a mixture of cobalt naphthenate and lead naphthenate in a proportion of 10 parts by weight cobalt naphthenate to 1 part by weight lead naphthenate. The thus-treated anode is then heated to effect substantially complete polymerization. The resultant anode is adapted for use in a chlorine-alkali electrode cell wherein it exhibits excellent properties.

In the practice of this invention it has been found that excellent results are obtained when a carbon electrode, typically a carbon anode as used in a chlor-alkali diaphragm cell, is impregnated with a polymerizable oil, such as the presently preferred linseed oil, tung oil, perilla oil, fish oil, safflower oil, soybean oil, oiticica oil, or dehydrated castor 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.

One qualitative test known to the art as indicative of the condition of a drying oil in the electrode and useful in the practice of this invention is the so-called "smoke test." This test involves heating an oil-impregnated electrode to a temperature at which the oil smokes. If no oil exudes from the electrode at this temperature, it is generally considered that the electrode is suitable for use in an electrolytic cell.

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 residue pitch. This mixing generally is carried out at an elevated temperature sufficient to melt the binder. The resultant mixture is then extruded and the thus-formed structure baked, typically at a temperature of about 1800° F., to remove volatile matter. 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 one or more times to a temperature in the range from 4150°–5000° F. At times, either a baked anode or graphitized anode can be further treated with pitch when it is desired further to improve the anode density and strength. Impregnation of the carbon anode with a drying oil can be accomplished in any conventional way, as by placing the anodes under vacuum and immersing the anodes while under vacuum into the desired impregnant. Illustrative of one specific method for impregnating a carbon anode is the following:

EXAMPLE II

A graphitized carbon anode is placed into an autoclave and a 28" Hg vacuum applied for 15 minutes to remove air from the anode pores. Linseed oil, heated to a temperature of 250° F., is then drawn into the autoclave and a pressure of 90 p.s.i.g. is applied for one hour. The excess linseed oil is then forced back into its heating tank and the anode surface is contacted eight times with superheated steam (300° F.) to remove surface retained oil.

EXAMPLE III

A carbon electrode is impregnated with a mixture of 220 cc. linseed oil (200 gms.), 3.3 gms. cobalt naphthenate, 10 gms. fumaric acid dissolved in 90 cc. dimethyl formamide, and 120 cc. acetone. The thus-impregnated electrode is then heated for 24 hours at 300° F. in a non-oxidative atmosphere to complete its preparation for use in a chlorine-alkali electrolytic cell.

EXAMPLE IV

Part A

A carbon electrode is impregnated with the following safflower oil composition:

Safflower oil	cc.	280
Acetone	cc.	120
Lead naphthenate	gms.	7.8
Cobalt naphthenate	gms.	3.1

by application of pressure to force this composition into the electrode while maintained in a vacuum. The thus-treated electrode is then exposed to steam for one hour and subsequently is heated to a temperature of 300° F. for 24 hours.

Part B

The electrode of Part A is placed in a hot (179°–184° F.) sodium chloride brine solution and gaseous chlorine introduced to simulate conditions existing in a chlorine-alkali cell. Using pH measurements to indicate the amount of oil leached from the electrode and chlorinated thus-forming HCl which lowers the pH, the following data illustrates the effectiveness of the practice of this invention.

Time (min.)	pH
0	5.0
30	4.2
60	4.0
90	4.0
120	4.0

Thus, it will be appreciated that an electrode of the present invention is quite stable and that little, if any, oil is leached therefrom.

EXAMPLE V

The procedure of Example IV is repeated using as a carbon impregnant the following composition:

Raw linseed oil	cc.	280
Acetone	cc.	120
Lead naphthenate	gms.	7.8
Cobalt naphthenate	gms.	3.1

Equally advantageous results are obtained.

It is to be understood that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited, since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

What is claimed is:

1. In the method of treating a porous carbon electrode including the steps of impregnating said electrode with a drying oil and heating the thus-impregnated electrode to effect polymerization of said drying oil, the improvement which comprises combining said drying oil with a mixture of lead and cobalt naphthenates, said mixture containing approximately from 28–91% of cobalt naphthenate and from 9% to 72% of lead naphthenate, the amount of said mixture being from approximately 4% to 10% of the weight of said drying oil.

2. The method of claim 1 wherein the amount of said mixture is 10% of the weight of said drying oil and the proportion of said lead naphthenate to said cobalt naphthenate is 10:1.

3. The method of claim 2 wherein said drying oil is linseed oil.

4. The method of claim 1 wherein the amount of said mixture is approximately 4% of said drying oil and the proportion of cobalt naphthenate is 2.5:1.

5. The method of claim 4 wherein said drying oil is linseed oil.

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