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TREATMENT OF ELECTRODES

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This invention concerns an improved method for impregnating porous articles of carbon, graphite, graphitized carbon, or the like, for the purpose of prolonging the useful life or other characteristics thereof; and is particularly applicable to the preparation of such articles to resist chemical attack, such as occurs when the same are used as electrodes in the electrolysis of alkali metal halides or for parts of electrolytic cells, etc. where subject to oxidizing action.

A carbon or graphite electrode, when used in a process for electrolyzing alkali metal chloride solutions, tends to absorb the salt solution, chlorine and oxygen are liberated within the voids of the electrode and as a result it becomes oxidized throughout and disintegrates. In order to prevent such action, it is general practice to impregnate the electrodes with oils, waxes or the like prior to using them in the aforementioned process. Such treatment increases the efficiency of the electrolytic process and materially lengthens the life of the electrodes themselves. While paraffin oil and waxes are generally used for impregnating electrodes, it has been found that better results are obtained when Chinawood oil and similar drying oils are substituted therefor.

Although treatment of electrodes, in the manner described above, decreases the diffusion of brine through the same and in general improves their quality, certain disadvantages result from such practice. During use of the so treated electrodes in the process for electrolyzing alkali metal chlorides, for instance, the oil with which they are impregnated becomes partially chlorinated and tends to swell, with the result that the electrodes sweat oil and at the same time crumble or wear away. The oil or wax so liberated from the electrodes proves further disadvantageous in that it tends to foul and obstruct the cell diaphragm, thereby interfering with the conduct of the process as a whole. However, after an electrode impregnated in the described manner has been largely worn away, the portion thereof remaining is found to be hard; it no longer sweats oil; it is impervious to brine; and further oxidation and distintegration of said remnant electrode proceeds with extreme slowness. This change in character of the electrode is believed to result from the oil remaining therein having become as completely chlorinated as is possible under conditions existing during such electrolysis, the previously mentioned disadvantages which occur during chlorination of said oil being thereafter absent. It is therefore desirable to change the character of impregnated electrodes to that last described before using the same.

An improved process for impregnating carbon electrodes, described by O. A. Laubi in United States Patent 1,779,242, consists in impregnating such electrodes with chlorinated hydrocarbons before using the same in electrolytic cells. By such treatment, further chlorination of the hydrocarbon oils used is said to proceed slowly, if at all, and the active life of such electrodes is lengthened appreciably. Another improved method of treating electrodes has been described in a co-pending application of R. M. Hunter and L. E. Ward, Serial No. 461,632, filed June 16, 1930. Briefly, their process consists in first impregnating carbon or graphite electrodes with a drying oil, e. g. Chinawood oil, then subjecting the impregnated electrodes to the action of chlorine over a considerable period of time. Although an electrode treated in such a manner often has an active life which exceeds that of one impregnated with Chinawood oil but not prechlorinated by as much as 50 per cent, the process is still disadvantageous in that the chlorination step proceeds slowly, generally requiring a period of several weeks or even months for appreciable chlorination of the impregnating oil to be effected. Furthermore, chlorination occurs most readily at the surface of the electrode and is liable to be non-uniform in depth of penetration. Therefore, electrodes treated in such a manner are not consistent in quality. In another co-pending application of R. M. Hunter and L. E. Ward, Serial No. 513,049, filed February 2, 1931, and entitled "Process for treating electrodes", a process is described whereby carbon or

graphite electrodes are impregnated with a prechlorinated drying oil such as Chinawood oil. Such treatment has been found to produce a product, uniform in quality, and superior in durability to electrodes prepared by the other mentioned processes.

The present invention involves a further modification of the above described processes for treatment of carbon electrodes, but is an improvement over all known methods in that the product obtained by the herein described process consists of a carbon and/or graphite electrode which has not only been impregnated with Chinawood oil but which has been further treated in such a manner as to both chlorinate and polymerize (or coagulate) the so used oil within the voids of the electrode. We have found that a carbon and/or graphite electrode, impregnated with Chinawood oil, when treated with a chloride ion containing solution of a strong mineral acid and at least one of the following group of salts:—ferric chloride, ferric sulfate, ferric nitrate, antimony pentachloride and titanium tetrachloride, is acted upon in such a manner that the oil therein is both polymerized and partially chlorinated, the result being that the electrode is rendered impervious to penetration by brine and very resistant to further action by chlorine. The present invention, then, consists of a process, and of the product from said process, hereinafter fully described and particularly pointed out in the claims, whereby a carbon and/or graphite electrode is impregnated with Chinawood oil, then the so used oil simultaneously chlorinated and polymerized within said electrode by means of a chloride ion containing solution of a strong mineral acid and a polymerizing salt. Free chlorine is preferably, but not necessarily, present in the above mentioned mineral acid solution during treatment of the impregnated electrode therewith.

Preliminary to the treatment of electrodes in the manner hereinafter described, tests were made to determine the effect of hydrochloric acid solutions of various salts upon Chinawood oil. Into a test tube were placed 10 cubic centimeters of a solution consisting of 50 per cent Chinawood oil and 50 per cent kerosene, by weight. To this solution were added 0.1 gram of ferric chloride, 0.5 gram of concentrated (37 per cent) hydrochloric acid and 0.5 gram of water. The mixture was thoroughly agitated, then permitted to stand at room temperature. In approximately 20 minutes the Chinawood oil was polymerized to a solid mass. The liquid remaining after such treatment was found to contain ferrous chloride, and analysis of the polymerized product proved it to have been partially chlorinated. By means of similar tests it was found that a similar chlorinated and polymerized product could be obtained by using ferric nitrate, ferric sulfate, or antimony pentachloride instead of the aforementioned ferric chloride. It was also found that titanium tetrachloride would produce the above described polymer, if used in a concentrated form.

Several of the various ways of applying the principle of our invention are described in the following examples. It is to be understood, however, that such examples are purely illustrative and are not to be construed as a limitation on the invention.

Example 1

A graphitized carbon plate was placed in a suitable air tight container and the latter evacuated to an absolute pressure of approximately 110 millimeters. Chinawood oil was then admitted to the container and the pressure thereon brought to and maintained at 125 pounds gauge during a period of 5 hours. The oil was then drained from the container and steam admitted thereto, in order to facilitate draining of excess oil adhering to the plate. (The oil content of a plate, at this point, is generally found to be approximately 9 to 12 per cent of the original weight of the latter, which means that approximately 50–80 per cent of the original voids in the plate are filled with oil). After treatment with steam, the container containing the graphite plate was again evacuated to an absolute pressure of approximately 110 millimeters and maintained at that pressure for about 2 minutes, then air admitted. The plate was removed from its container and plunged, while hot, into a solution of ferric chloride in hydrochloric acid where it was permitted to cool to room temperature, then removed and dried. The plate was then ready for use as an electrode in the previously mentioned electrolytic process.

Example 2

A graphitized carbon plate was treated in a way similar to that described in Example 1, except that chlorine was passed through the solution of ferric chloride in hydrochloric acid during the time the impregnated plate was immersed and cooling therein. It was found, upon analysis of various cuts from cross-sections both of this plate and of the plate described in Example 1, that in the present example the polymerized oil was chlorinated at a greater depth from the surface of the electrode and more uniformly than it was in the product obtained according to the method described in Example 1.

Electrodes, prepared according to our method, have been found to be impervious to penetration by brine and to be very resistant to further action by the chlorine liberated during the aforementioned electrolytic process. Tests made indicate that they have a longer active life than do such electrodes treated by any previously described process.

In the claims it shall be understood that the term "carbon and/or graphite" shall be used to characterize an electrode or article composed chiefly of carbon, graphite, or graphitized carbon.

Other forms of applying the principle of our invention may be employed instead of the ones here explained, change being made in the method or composition, provided the steps or ingredients stated by any of the following claims or the equivalent of such stated steps or ingredients be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. In a method of treating a carbon and/or graphite article, the steps which consist in impregnating said article with Chinawood oil and then simultaneously chlorinating and polymerizing said oil by means of a chloride ion containing solution of a strong mineral acid and a polymerizing salt.

2. In a method of treating a carbon and/or graphite electrode, the steps which consist in impregnating said electrode with Chinawood oil, then further subjecting the thus impregnated electrode to the action of a hydrochloric acid solution containing at least one of the following group of salts:—ferric chloride, ferric sulphate, ferric nitrate, antimony pentachloride, titanium tetrachloride.

3. In a method of treating a carbon and/or graphite electrode, the steps which consist in impregnating said electrode with Chinawood oil, heating the impregnated electrode with steam, then cooling said electrode in a hydrochloric acid solution containing free chlorine and also containing at least one of the following group of salts:—ferric chloride, ferric sulphate, ferric nitrate, antimony pentachloride, titanium tetrachloride.

4. In a method of treating a carbon and/or graphite electrode, the steps which consist in impregnating said electrode with Chinawood oil, heating the impregnated electrode with steam, then cooling said electrode in a hydrochloric acid solution containing at least one of the following group of salts:—ferric chloride, ferric sulphate, ferric nitrate, antimony pentachloride, titanium tetrachloride.

5. In a method of treating a carbon and/or graphite electrode, impregnated with Chinawood oil, the step which consists in simultaneously chlorinating and polymerizing said oil by means of a chloride ion containing soluton of a strong mineral acid and a polymerizing salt.

6. In a method of treating a carbon and/or graphite electrode, the step which consists in subjecting such an electrode, impregnated with Chinawood oil, to the action of a hydrochloric acid solution containing at least one of the following group of salts:—ferric chloride, ferric sulphate, ferric nitrate, antimony pentachloride, titanium tetrachloride.

7. In a method of treating a carbon and/or graphite electrode, the steps which consist in treating such an electrode, impregnated with Chinawood oil, with steam, then cooling said electrode in a hydrochloric acid solution containing free chlorine and also containing at least one of the following group of salts:—ferric chloride, ferric sulphate, ferric nitrate, antimony pentachloride, titanium tetrachloride.

8. In a method of treating a carbon and/or graphite electrode, the steps which consist in treating such an electrode, impregnated with Chinawood oil, with steam, then cooling said electrode in a hydrochloric acid solution containing at least one of the following group of salts:—ferric chloride, ferric sulphate, ferric nitrate, antimony pentachloride, titanium tetrachloride.

9. In a method of treating a carbon and/or graphite electrode, the steps which consist in impregnating said electrode with Chinawood oil, then treating the so impregnated electrode with steam, and finally cooling the electrode in a hydrochloric acid solution containing chlorine and ferric chloride.

10. In a method of treating a carbon and/or graphite electrode, the steps which consist in impregnating said electrode with Chinawood oil, then treating the so impregnated electrode with steam, and finally cooling the electrode in a hydrochloric acid solution containing ferric chloride.

11. As a product of manufacture, a carbon and/or graphite article impregnated with a polymerized form of Chinawood oil which is at least in part chlorinated.

12. As a product of manufacture, a carbon and/or graphite electrode impregnated with a polymerized form of Chinawood oil which is at least in part chlorinated.

Signed by us this 23rd day of May, 1931.

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