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IMPREGNATED CARBONACEOUS ELECTRODE AND METHOD OF MAKING THE SAME

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This invention relates to a process for treating electrodes and more particularly relates to an improved process for treating carbonaceous anodes for use in alkali chlorine cells of the diaphragm type.

A common type of cell used for the electrolytic decomposition of water-soluble alkali-metal brine solutions, such as chlorides of potassium and sodium, as for the production of chlorine and sodium hydroxide, and liberation of hydrogen, are those referred to as diaphragm cells. In diaphragm type electrolytic cells, the anode compartment is separated from the cathode compartment by a permeable diaphragm, preferably of asbestos. The brine solution is introduced into the anode compartment, where it comes into contact with the anodes, and is caused to percolate through the diaphragm into the cathode compartment where it comes into contact with the cathodes. When an electric current is passed between these electrodes, chlorine is liberated at the anodes and an alkali metal hydroxide is formed at the cathodes, with the liberation of hydrogen gas.

Carbonaceous electrodes when used in the above type cell as anodes tend to absorb the alkali metal chloride brine solution. Upon subsequent passage of an electric current, chlorine and oxygen are liberated within the voids of the anodes, oxidizing them throughout until they ultimately reach a point of disintegration. In order to prevent this action, it has become the practice in the art to impregnate carbonaceous anodes with an oil, such as linseed oil, prior to their use in an electrolytic cell. Driers such as cobalt, lead and manganese are generally incorporated in the oil to accelerate drying and hardening. The use of linseeed oil in conjunction with a dryer decreases the diffusion of the brine solution throughout an anode and generally improves its quality, but unfortunately certain disadvantages may be encountered in practice. The linseed oil within an anode may dry or harden rather slowly and non-uniformly, due to the inaccessibility of air into the anode's inner structure, and occasionally an anode may be placed in service wherein oil is only partially dried or hardened. If such is the case, the non-hardened portion of the linseed oil will leach out of the anode and become chlorinated. Chlorination of the linseed oil not only directly reduces the chlorine output of the cell, but also results in finely divided chlorinated oil being deposited on the permeable diaphragm, thereby rapidly reducing the brine flow therethrough, usually resulting in complete plugging of the diaphragm in a short time.

Another inherent disadvantage in the chlorination of the linseed oil is the formation of hydrochloric acid as a by-product in the anolyte which will attack the asbestos diaphragm causing the release of basic magnesia to further plug and foul the diaphragm. Even partial stoppage of fluid flow through the diaphragm will result in high brine levels in the anolyte compartment unless the rate of brine flow into the anolyte compartment is reduced, in which case the efficiency of the cell is also reduced.

A still further disadvantage which may be encountered if linseed oil is used as an impregnant is that a non-conducting skeletal layer of linseed oil may form during use on the surface of the anode, causing anode voltage and consumption rate to rise concurrently.

The principal object of the invention is to provide an

impregnant for carbonaceous electrodes that are used as anodes in alkali chlorine electrolytic cells which will substantially reduce deterioration of such anodes due to the attack of chlorine and oxygen.

An equally important object of the invention is to provide an impregnant for carbonaceous anodes which adequately protects the life of such anodes without causing, by its presence, an undue deleterious effect on the performance of an electrolytic cell.

Broadly stated, the objects of the invention are accomplished by impregnating a carbonaceous electrode with a resin which consists of a furfuraldehyde-ketone condensation product composed of a mixture of hydrogenated mono- and di-furfuryl ketones, and preferably, a small amount of cobalt nitrate.

The exact amount of the resin that is impregnated in a carbonaceous electrode is not critical to the successful practice of the invention and is generally determined by the amount that can be introduced into the pores of the electrode. If the electrode is formed of normal density graphite a total weight pickup of resin in the range from 11 to 16.8 percent is preferred. If the graphite electrode is of a denser structure such as that obtained by treating the electrode with pitch prior to the graphitization, the above range is cut approximately in half,. The percentage of impregnated cobalt nitrate used in the preferred embodiment of the invention is in the range of from .01 to 0.1 percent by weight of the impregnated anode.

More specifically in the preferred embodiment of the invention, cobalt nitrate may be dissolved in an alcohol which is miscible with the furfuraldehyde-ketone condensation product resin, and this is added, in an appropriate amount to the resin to attain the desired cobalt concentration, the alcohol serving as a mutual solvent. Shortly before impregnation a suitable polymerizing catalyst is added to the solution for purposes of setting the resin. Suitable catalysts which may be employed in the practice of the invention comprise diethyl sulfate and other acid catalysts which are soluble in the resin including toluene sulfonic acid and mono-alkyl and mono-dialkyl acid orthophosphates. This solution is then impregnated within a carbonaceous electrode by the alternate application of vacuum and pressure, and the impregnated electrode is cured under nitrogen pressure by the application of heat.

In the practice of the embodiment of the invention wherein no cobalt nitrate is used, the polymerizing catalyst is added directly to the resin shortly before impregnation, under normal circumstances. If desired, one of the suitable catalysts may be added to the resin at any time if the resin is kept under refrigerated conditions until shortly before it is impregnated within an electrode.

The addition of a small amount of cobalt nitrate in the preferred embodiment of the invention is not for the purpose of accelerating the drying of the impregnated resin as taught in the prior art, but for its function as a catalyst in decomposing to a chloride and oxygen the hypochlorite formed in the anolyte liquor of an alkali chlorine diaphragm type electrolytic cell. Hypochlorite normally decomposes to form a chlorate which will strongly attack a carbonaceous electrode, particularly at the temperatures normally employed in alkali chlorine cells of the diaphragm type. However, while cobalt nitrate is effective in reducing anode attack, it alone is not a satisfactory impregnant for it may leach out of the electrode in the mildly acid anolyte liquor over an extended period of time and cause excessive oxygen build-up in the anode compartment. The combination with the furfuraldehyde-ketone condensation product resin controls the release of the cobalt nitrate to the anolyte liquor so that at no time is there an excessive cobalt nitrate concentration.

Performance tests run in laboratory alkali chlorine dia-

phragm cells gave the results tabulated in the table below, and conclusively prove the success of the subject invention. A description of such laboratory cells is given by N. J. Johnson, Trans. Electrochem. Soc. 86, 127–142 (1944).

The electrodes which were tested to give the results reported in runs 6–8 and 10 in the table were prepared by impregnating them with the furfuraldehyde-ketone condensation product resin to which an alcohol, containing cobalt nitrate, was added in appropriate amounts for the desired cobalt concentrations. A 10 percent diethyl sulfate aqueous solution was used as a catalyst for setting the resin. Following a vacuum-pressure impregnation, the resin was cured at 225° C. under 100 pounds of nitrogen pressure, for four hours. The electrode which was tested to give the results of Run 12 was impregnated in the same manner with a solution of the resin and a 10 percent diethyl sulfate aqueous solution. Each of the electrodes tested in the remaining runs was also impregnated by conventional vacuum-pressure techniques.

In the table, average caustic color is reported in units which represent the percentage of monochromatic light (480 angstrom units) transmitted through the aqueous caustic solution of the cell as compared with pure distilled water.

cobalt nitrate, it serves to reduce anode consumption and sludge accumulation far better than any of the impregnants of the prior art.

Experimental tests have indicated that the furfuraldehyde-ketone condensation product resin is chlorinated to some extent in the practice of the invention. Fortunately however, these chlorinated products are such that they are retained within the anode and do not form a skeletal layer which increases voltage and anode consumption. As shown in the table, the final apparent density of the anode is always somewhat higher than the initial apparent density due to chlorination of the resin. The exact opposite result is experienced when linseed oil or furfural is used as the impregnant, either alone or in conjunction with cobalt nitrate. In contrast to the serious difficulties encountered in the operation of electrolytic cells of the diaphragm type when linseed oil becomes chlorinated, the chlorinated products of the furfuraldehyde-ketone condensation product resin which remain in the anode are beneficial in that they tend to further restrict diffusion of the alkali metal brine throughout the inner structure of the electrode. Moreover, due to the chemical structure of the furfuraldehyde-ketone condensation product resin there are no unsaturated bonds for chlorine attack or hydrochloric acid formation as there is with linseed oil. Typical anolyte pH values illustrative of this fact shortly after cell start up are 3.8 when the resin is used, and 2.0 when linseed oil is used.

Table

Run	Current density, amperes per square inch	Impregnant	Percent total weight pickup	Percent cobalt nitrate	Consumption per 1,000 ampere hours		Sludge (percent of total weight loss)	Average, volts	Average caustic color	Apparent density	
					Grams	Cubic centimeters				Initial	Final
1	0.5	None			10.60	6.54	9.8	2.89	49.9	1.548	1.474
2	.5	Linseed oil	8.0	0.0034	6.49	3.63	11.4	3.07	91.3	1.703	1.669
3	.5	do	8.0	0.0034	6.29	3.60	10.15	3.07	92.3	1.664	1.633
4	.5	do	8.0	0.0034	6.31	3.88	7.23	3.11	91.2	1.691	1.660
Average	.5		8.0	0.0034	6.36	3.70	9.59	3.08	91.6	1.686	1.664
5	.5	Furfural	5.7	0.028	8.02	4.09	7.52	2.96	78.8	1.657	1.522
6	.5	Furfuraldehyde-ketone-condensation product resin.	14.4	0.027	5.34	3.20	2.10	3.04	89.1	1.719	1.736
7	.5	do	14.6	0.053	4.40	2.70	1.56	3.02	90.9	1.734	1.761
8	.5	do	11.5	0.077	4.72	2.89	4.24	3.02	93.3	1.688	1.703
Average	.5		13.5	0.052	4.82	2.97	2.63	3.03	91.1	1.714	1.733
9	.8	Linseed oil	7.7	0.0032	10.96	6.43	5.30	3.35	80.7	1.683	1.669
10	.8	Furfuraldehyde-ketone-condensation product resin.	16.4	0.028	8.36	4.68	2.92	3.39	91.3	1.781	1.788
11	.5	Furfural	4.1		10.79	5.94	7.49	2.94	60.3	1.659	1.633
12	.5	Furfuraldehyde-ketone-condensation product resin.	14.5		6.02	3.55	1.50	3.01	81.5	1.739	1.756

A study of the table clearly illustrates the superiority of the furfuraldehyde-ketone condensation product resin and cobalt nitrate impregnation as opposed to the impregnants of the prior art. On the average, in electrolytic cells of the diaphragm type having a current density of 0.5 ampere per square inch, the use of the preferred impregnant of the invention as compared to an impregnation of linseed oil and cobalt nitrate, reduced anode consumption 24.2 percent by weight and 19.7 percent by volume. Sludge accumulation, which is partially the cause of diaphragm fouling, was reduced by more than 72 percent. Likewise, in an electrolytic cell having a current density of 0.8 ampere per square inch, as used commercially, anode consumption was reduced 23.7 percent by weight and 27.2 percent by volume. Moreover, sludge accumulation was reduced 44.9 percent and caustic color was improved by 11.9 percent. Run number 5, wherein an electrode impregnated with furfural and cobalt nitrate was tested, clearly indicates that this is not a satisfactory impregnant for the results are far inferior to those that were obtained with the preferred impregnant of the invention.

Run number 12, clearly shows that while an impregnation with furfuraldehyde-ketone condensation product resin alone is not quite as good in all respects as an impregnation with both the resin and a small amount of

The advantages and novel contributions made to the art by the above outlined invention may be summarized as follows:

(1) A 15 to 30 percent reduction in anode consumption rate resulting in longer anode life and less frequent rebuilding of the cells.

(2) The use of a cured resin impregnant making the probability of acid formation through reaction with chlorine much less than with an unsaturated impregnant such as linseed oil. The absence or reduction of acid in the anolyte will retard diaphragm attack and subsequent fouling.

(3) A reduction in sludge accumulation.

(4) An anode impregnant whose chlorinated products tend to remain in the anode increasing its density which thereby aids in preventing the leaching out of any cobalt nitrate that may be incorporated as a constituent of the impregnant. The retention of the chlorinated products also aids in keeping the chlorine gas stream free from contaminating materials.

(5) A treatment which will provide a more uniform and controlled electrode in which aging is not a factor.

What is claimed is:

1. A method of enhancing the resistance to chemical attack of a carbonaceous anode in brine electrolysis, which method comprises impregnating said anode with (*a*) a liquid, polymerizable furfuraldehyde-ketone condensation product comprised of a mixture of hydrogenated mono- and di-furfuryl ketones and (*b*) a polymerizing catalyst therefor dissolved therein, said catalyst being selected from the group consisting of diethyl sulfate, toluene sulfonic acid and mono-alkyl and mono-dialkyl acid orthophosphates; and heating the impregnated anode so produced to resinify and cure said product in situ, the quantity of said product in said electrode being such as to provide about 5.5% to 16.8% resin in said anode by weight of said anode.

2. A method as defined by claim 1 in which impregnation of said anode by said furfuraldehyde-ketone condensation product is achieved by the alternate application of vacuum and pressure, said selected catalyst is diethyl sulfate, and said resinifying and curing step is conducted at a temperature of about 225° C. for about four hours.

3. A method as defined by claim 1 in which said furfuraldehyde-ketone condensation product and said selected catalyst are dissolved in alcohol and said alcohol solution also contains cobalt nitrate in a quantity sufficient to provide 0.01% to 0.1% cobalt nitrate in said anode by

weight of said anode after said resinifying and curing step.

4. A method as defined by claim 3 in which said selected catalyst is an aqueous solution of diethyl sulfate and said resinifying and curing step is conducted at about 225° C. under an atmosphere of nitrogen.

5. A carbonaceous electrode being resistant to chemical attack in the electrolysis of brine, said electrode having within its pores a resinified and cured furfuraldehyde-ketone condensation product composed of a mixture of hydrogenated mono- and di-furfuryl ketones in a proportion of about 5.5% to 16.8% by weight of said electrode.

6. An electrode as defined by claim 5 also containing cobalt nitrate in a proportion of about 0.01% to 0.1% by weight of said electrode.

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