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**PURIFICATION OF AQUEOUS CAUSTIC SOLUTIONS**

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This application is a continuation-in-part of our previously filed application, Serial No. 153,062, filed November 17, 1961, now abandoned.

This invention relates to an electrolytic apparatus and method for the treatment of aqueous caustic solutions thereby to remove metal ion impurities and improve the color of the solution.

In many industrial applications, aqueous caustic solutions are required having a high degree of purity. Often, metal ions enter the solutions during the process of manufacture, during transport or in various other ways. These metal ions may, in certain instances, cause a deterioration in color of the aqueous solution. Further, in many processes, the presence of metal ion impurities renders the aqueous caustic solution useless for the intended purpose.

It is an object, then, of the present invention to provide a method and apparatus whereby substantially all of the metal ion impurities may be removed from an aqueous caustic solution.

Numerous methods have been proposed for the removal of metal ions from aqueous caustic solutions. Among such methods are filtration, precipitation, adsorption, and the like. These methods are generally expensive and inefficient relative to the present method.

We have discovered a method and apparatus whereby metal ion content of aqueous caustic solutions may be reduced to substantially nil in a simple one-step operation. In accordance with our invention, an aqueous caustic solution containing metal ion impurities is subjected to electrolytic treatment in a cell having as its cathode a fluid permeable pad of fine strands of electric current conducting material.

In the electrolytic processing art, it is well known that when an aqueous solution containing metal ions is subjected to an electric current, that the metal ions will tend to plate out on the cathode. It is another well recognized phenomenon within this art that the predominant plating out of metal on the cathode takes place at the portion of the cathode closest to the anode. It is for this reason, that most cathodes used for the plating of metal ion from solution are designed so that a maximum amount of surface area is in a plane normal to the line between the anode and cathode of the cell. Because of this characteristic of plating at the point closest to the anode, most cathodes are of a flat, thin plate or screen-like design since little or no metal plating would occur at any distance from the surface closest to the anode. It was, therefore, unexpected that a mesh pad of wire or other conducting material, when employed as a cathode in accordance with the present invention, would receive a relatively uniform plate of metal, from the metal ion containing solution, over the entire surface area of said pad. Since the surface area per unit volume of the cathodes employed in the present invention is substantially greater than that of cathodes having a thin design, greater efficiency in metal ion removal by plating may be obtained. Further, more metal ion may be removed from the solution before replacement or cleaning of individual cathodes becomes necessary.

The term "metal ion impurities" as used herein refers to those metal ions belows aluminum in the electromotive

series of elements which can be electroplated from aqueous solutions i.e. those metals having an electrolytic potential less than that of aluminum. These metals include zinc, chromium, iron, cadmium, cobalt, nickel, tin, lead, antimony, copper, mercury, silver, lead and gold.

Cathodes appropriate for use in the present invention are greater than one quarter inch in thickness and usually from one quarter to twelve inches in thickness, the thickness being measured along the line between the anode and cathode, and made of strands of a current conducting material which has a cross-sectional area equivalent to wire having a diameter of from 0.001 to 0.03 inch in diameter. The surface area to volume ratio of the appropriate cathodes for use in the present invention is generally from about 50 to about 600 square feet of surface area per cubic foot of cathode volume. The cathodes are made of electric current conducting strands which are resistant to caustic under cell operating conditions. Generally metallic wire or strands of nickel and nickel alloys, stainless steels, mild steel and silver are used.

Aqueous caustic solutions which may be purified by the method and apparatus of the present invention are those which contain from about 0.25 to about 500 parts per million of metal ion impurities. Solutions containing less than about 0.25 part per million of metal ion impurities may be purified by the method and apparatus of the present invention but it is usually not necessary to do so. When purification of solutions containing more than about 500 parts per million of metal ion impurities is attempted by the method and apparatus of the present invention, the problem of throwing power presents itself. Solutions having high concentrations (over about 500 parts per million) of metal ion impurities tend to behave such that plating occurs only at that portion of the cathode closest the anode, thus losing the advantages of the present method. While the process of the present invention is applicable to caustic soda solutions of various concentrations it is particularly useful for the purification of aqueous solutions containing greater than 40% caustic soda.

In practice, the aqueous caustic solution which contains the metal ion impurity is generally passed through the cell in such a manner as to flow through the mesh pad cathode. Alternately, the cathode may be agitated as by vibrating or reciprocating, in order to increase the solution to cathode contact. Also, the number of cathodes and anodes may be multiplied in order to assure maximum solution-cathode contact.

In general, for best operations, the current densities to be employed are generally in the range of from about 1 to about 6 amperes per square foot of cathode surface area. The particular voltage employed to obtain a desired cathode current density normally depends upon the cell design but is usually low, being in the range of from about 1.6 to about 4 volts per cell. If desired, a plurality of cathodes and anodes may be operated in series by employing a higher voltage across the series. The preferred current densities are generally dependent on the individual solution to be treated. Ordinarily, the current density is adjusted during operation to achieve the desired results. Preferred solution temperatures for operation of the present invention are usually in excess of 25 degrees C. but preferably range from about 40 degrees centigrade to the boiling point of the aqueous solution. Temperature is not particularly critical, the only requirement being that the solution be fluid at the temperature employed. The optimum temperature may vary somewhat with the particular nature and concentration of the solution and the design of the cell.

After a period of use, the cathodes may be simply discarded, or treated to recover or remove the metal which

has plated on them. In such treatment, it is common to take a solution which will preferentially dissolve the plated metal.

A better understanding of the present invention may be had in light of the following examples which are set forth to illustrate, and are not to be construed to limit the present invention.

#### Example 1

A pilot plant test was run with a cell having three cathodes of mesh pads one-inch thick. Each mesh pad had a stiffener for support. The stiffener was an eight-mesh nickel screen to which an electrical connection was made. The pads, one foot square, were constructed of woven nickel wire of approximately .006 inch in diameter and had a wire surface to pad volume ratio of 288 square feet of surface area per cubic foot of cathode volume. Anodes of an eight-mesh wire screen fabricated of 0.032 inch diameter nickel wire were inserted between the cathodes and at each end of the cell.

A fifty percent sodium hydroxide solution at 102 degrees centigrade was passed through the cell at a rate of 1.6 gallons per minute. The voltage applied was 2.5 volts, at which voltage a cathode current density of 2.1 amperes per square foot was obtained. The sodium hydroxide product charged was slightly blue in color and contained about 35 parts per million of iron based on the sodium hydroxide content. After passage through the cell, the sodium hydroxide solution contained four parts per million of iron on the same basis and had attained a water-white color. Plating of iron occurred throughout each cathode. Analysis of the deposit formed on the cathodes showed that iron, copper, nickel and lead had been removed from solution.

#### Example 2

A cell having rotating cathode pads was employed. The cathode pads were circular discs having an overall diameter of about 12 inches and a center aperture of 2 inches in diameter. These cathodes were constructed with pads of one-half inch thickness of mesh material of the type described in Example 1 on each side of the five-eighth inch mesh nickel screen stiffener. The cathodes were attached to a five-eighth inch vertical shaft and rotated. A total of eight cathodes were thus assembled on the shaft. Anodes, also circular in shape and with circular central apertures, were made of ten gauge nickel plate. These were inserted between the cathode surfaces. The anodes were stationary and assembled inside the cell which was a vertical cylindrical vessel of approximately fourteen inch internal diameter.

Sodium hydroxide solution to be treated was introduced into the cell at the bottom and discharged at the top. In one run, sodium hydroxide solution was fed to the cell at the rate of one gallon per minute, contained fifty percent by weight of sodium hydroxide and was at a temperature of 58 degrees centigrade. The solution also contained about 31 parts per million of iron, based upon anhydrous sodium hydroxide content. The cathode surfaces were rotated at a rate of about 135 revolutions per minute and the cathode current density was about 2.1 amperes per square foot of total cathode surface area. The product obtained from the cell contained less than one part per million of iron, a greater than 96 percent removal of the iron present. Plating of iron occurred throughout the cathode.

#### Example 3

Cathodes made of pads similar to those in Example 1 were reciprocated in a cell in an up and down direction at a rate of from about 130 to about 240 cycles per minute, the amplitude of the reciprocating motion being from about one-half to about one-inch. When an aqueous sodium hydroxide solution containing about 35 parts per million iron was passed through the cell,

results similar to those set forth in Examples 1 and 2 were obtained. The removal of iron from the aqueous sodium hydroxide solution was highly efficient. Plating was observed to be uniform throughout the cathodes.

#### Example 4.—Comparative

Mesh cylinders were prepared from 2-inch by 24-inch strips of nickel wire mesh, the wire having a diameter of 0.007-inch, rolled into a cylinder one and five-eighth inches by 2 inches. Electrical contact with the cylinder was established using an insulated nickel wire connected to the bottom of the mesh cylinder. The mesh cylinder was inserted in a beaker such that the bottom of the mesh cylinder almost touched the bottom of the beaker. An anode was made of a circular section of nickel screen one and one-half inches in diameter, the screen being of the same material used to fabricate the mesh cylinder cathode. The anode was positioned slightly above the cathode in the beaker and electrical contact was established therewith in a manner similar to that employed with the cathode. In operation, the beaker was filled with test solution, current was passed through the solution for an appropriate amount of time, and the results observed.

About 300 milliliters of an aqueous solution containing fifty percent NaOH and five percent copper was used as the electrolyte. An average of 0.5 ampere was passed through the solution for about ten minutes. The entire run was conducted at about 70 degrees centigrade. At the end of this time the mesh cathode had copper plated only on the portion which faced the anode.

#### Example 5

An aqueous solution of 50 percent NaOH containing about 100 parts per million of copper was electrolyzed in the apparatus and under substantially the conditions described in Example 4. Uniform deposition of copper was obtained throughout the wire mesh cathode.

#### Example 6

Employing an apparatus substantially as described in Example 4 an aqueous solution containing 50 percent NaOH and 100 parts per million zinc was electrolyzed at 0.5 ampere for 10 minutes at a temperature of about 70 degrees centigrade. The cathode was removed from the bath and washed with a copper solution in order to show where zinc had been plated. A copper sulfate wash of an unplated nickel cathode has no effect but it will color one which has been plated with zinc or iron. By observing the color due to the copper solution wash, it was observed that zinc had plated throughout the wire mesh cathode in a uniform manner.

#### Example 7

In substantially the same manner as Example 6, a 50 percent aqueous sodium hydroxide bath containing about 100 parts per million iron was electrolyzed at 70 degrees centigrade. Electrolysis was carried on at about 0.5 ampere for 10 minutes. After electrolysis the cathode was removed and washed with a copper-containing solution in order to expose the iron deposited areas. Examination of the washed cathode indicated that uniform plating throughout the wire mesh cathode had occurred.

#### Example 8.—Comparative

In substantially the same manner as Examples 6 and 7, a 50 percent aqueous sodium hydroxide solution containing about 2 percent zinc was electrolyzed at 70 degrees centigrade. Electrolysis was carried on at about 2 amperes for about 3 minutes. Higher amperage than was previously used was employed due to the higher activity of the zinc. Washing with copper solution and examination of the cathode after electrolysis indicated that only the portion of the pad closest the anode contained zinc deposit.

Example 9

A group of nickel mesh cathodes as hereinbefore described were subjected to electrolysis at about one ampere for 10 minutes in various solutions with the following results:

Electrolysis of an aqueous solution containing 50 percent NaOH and 0.5 percent copper resulted in deposition only at the portion of the cathode closest to the anode.

Electrolysis of an aqueous 50 percent sodium hydroxide solution containing 100 parts per million of iron resulted in uniform deposition of iron throughout the wire mesh cathode.

Electrolysis of an aqueous solution containing 50 percent sodium hydroxide and 100 parts per million copper resulted in uniform deposition of copper throughout the wire mesh cathode.

Various modifications may be made in the present invention without departing from the spirit or scope thereof, and it is to be understood that we limit ourselves only as defined in the appended claims.

We claim:

1. A method of purifying caustic solutions containing metal ion impurities, which comprises providing an anode, providing a mesh cathode of an electric current conducting metal which is resistant to caustic under electrolytic cell operating conditions, said cathode being from one quarter to four inches in thickness, fabricated of strands having a cross sectional area equivalent to wire of .001 to 0.03 inches in diameter and a surface to volume ratio of from 50 to 600 square feet of area per cubic foot in volume, providing a caustic solution containing a maximum of 500 parts per million metal ion impurities, and subjecting said solution to electrolysis, thereby depositing said metal ion impurities through said cathode.

2. The method as defined in claim 1 wherein the aqueous caustic solution is aqueous sodium hydroxide.

3. The method of claim 2 in which the cathode is made of nickel.

4. The method of claim 2 in which the cathode is an alloy of nickel.

5. The method of claim 2 in which the cathode is a stainless steel.

6. The method as defined in claim 1 wherein the metal ion impurity is iron.

7. The method as defined in claim 1 wherein the metal ion impurity is copper.

8. The method as defined in claim 1 wherein the metal ion impurity is zinc.

9. The method as defined in claim 1 wherein the metal ion impurity is iron and is present at a maximum of about 100 parts per million Fe.

10. The method as defined in claim 1 wherein the metal ion impurity is copper and is present at a maximum of about 100 parts per million Cu.

11. The method as defined in claim 1 wherein the metal ion impurity is zinc and is present at a maximum of about 100 parts per million Zn.

12. The method as defined in claim 1 wherein the metal ion impurity is iron and is present in an amount of about 35 parts per million Fe.

13. The method as defined in claim 1 wherein a reciprocating motion is imparted to the cathode during electrolysis.

14. The method as defined in claim 1 wherein the cathode is caused to revolve during electrolysis.

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