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FLUORINE-CONTAINING ELECTROLYTE FOR ELECTROLYTIC CUTTING OF METALS

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This invention relates to an electrolyte useful in a process for electrolytic cutting of metals.

The difficulty and expense of cutting tough and hard metals and alloys has led to interest in electrolytic methods for accomplishing operations comparable to sawing, milling, drilling and other machining processes. Metals can be dissolved and removed by electrolytic action when an electrode connected as a cathode is maintained a short distance from a workpiece connected as an anode, and a high amperage electric current is passed between cathode and anode. During passage of the electric current the working end of the cathode and the adjacent surface of the workpiece are immersed in an aqueous electrolyte which is circulated at a high velocity through and around the working site. Rapid circulation of the electrolyte is desirable to cool the cathode and workpiece, to prevent boiling and volatilization of the electrolyte due to heat generated by the electric current passage, and to provide a supply of ions for electrolysis. The basic process is relatively simple but adaptation for commercial use has been hampered by several serious problems. Difficulty has heretofore been encountered in controlling the action to remove the metal from only the desired area of the workpiece. In addition, the cutting action appears to be not necessarily by nature uniform; and pitting, grooving and discoloration of the workpiece surface has been encountered as well as indiscriminate metal removal resulting in rounded edges and lack of ability to produce clean, straight cuts. Ideally an electrolytic cutting process should remove metal cleanly and evenly from the precise area desired and leave a smooth and preferably polished surface on the workpiece.

Workpieces of reactive metals, such as titanium and zirconium, have been more difficult to handle than the more common metals, such as iron and steel; pitted and discolored surfaces being obtained in many cases. It has also been difficult heretofore to produce smooth, even cuts on complex and high alloy steels and the so-called super alloys. An electrolyte which could be successfully employed on reactive metals as well as ferrous metals, high alloy steels and the so-called super alloys would be extremely advantageous.

It is therefore an object of this invention to provide an improved electrolyte for use in electrolytic cutting of metals. Another object of this invention is to provide an electrolyte useful in electrolytic cutting of metals which will promote even and controllable removal of metal and leave a clean, smooth finish on the workpiece. Another object of this invention is to provide an electrolyte useful for electrolytic cutting of a variety of metals including reactive metals such as titanium and zirconium. These and other objects of this invention will be apparent from the following description thereof.

This invention in its broad aspects contemplates an electrolyte for electrolytic cutting of a metallic workpiece which consists essentially of sodium chloride, potassium chloride, or ammonium chloride; a small proportion of sodium fluoride; a small proportion of a complexing agent selected from the group consisting of tartaric acid, formic acid, citric acid, and succinic acid; with the balance water. Optionally, the electrolyte may

contain a small amount of hydrogen peroxide and a small amount of nitric acid.

The salt selected from the group consisting of sodium chloride, potassium chloride, and ammonium chloride is present in the electrolyte in amount more than 5% by weight and up to saturation. This salt appears to function principally as an electric current carrying medium when ionized in solution and the amount present is not critical within the range stated. More than 5% is required to provide sufficient current carrying capacity to the electrolyte and the upper limit of its content is regulated by its solubility in the solution. Sodium chloride, potassium chloride, and ammonium chloride are soluble in water at normal room temperature in amount somewhere between 20 and 30% by weight, the precise figure will depend, as is obvious to those skilled in the art, on various factors including the concentration of other salts and ions present in the electrolyte, and the precise temperature.

Sodium fluoride is present in the electrolyte of this invention in amount from 0.2 to 2% by weight. The sodium fluoride content appears to promote clean and effective electrolytic cutting without formation of discoloration on the surface of the metal being cut, and this compound also appears to prevent formation of a black scum on the metal surface. Less than 0.2% of sodium fluoride will not provide sufficient fluoride ions in the electrolyte to give the desired improvement in cutting conditions, and more than 2% sodium fluoride will increase the corrosive nature of the electrolyte to an extent that some chemical solubility of the metal workpiece in the electrolyte solution may result.

The complexing agent is an acid selected from the group consisting of tartaric acid, formic acid, citric acid, and succinic acid, and is present in the electrolyte of this invention in amount from 1 to 5% by weight. This ingredient appears to promote suspension or solution of salts or compounds in the solution during the electrolytic cutting operation. At least 1% of the complexing agent appears necessary to produce this effect and amounts of 5% provide no additional benefit, and result in uneconomical and wasteful addition of an excess which provides no increase in desirable operating conditions. The complexing agent represents one of the more expensive ingredients in the electrolyte.

Optionally, the electrolyte of this invention may contain up to 4% by weight of a 30% aqueous solution of hydrogen peroxide. Hydrogen peroxide is commercially available as a 30% aqueous solution and amounts up to 4% have been found to eliminate a granulation or precipitation of solid salts or compounds in the electrolyte which occasionally and under certain conditions may interfere with the electrolytic action between the electrode and the workpiece surface. More than 4% by weight of hydrogen peroxide solution will provide no increased benefit and is wasteful of this relatively expensive ingredient.

Additionally, the electrolyte of this invention may contain up to 5% by weight of commercial 70% nitric acid. The presence of nitric acid in amount up to 5% has been found to provide somewhat smoother electrolytic cutting action to promote production of clean, uniform surfaces on the cut areas of the workpiece. More than 5% nitric acid should not be employed in the electrolyte since this raises the hydrogen ion content to a point where undesirable corrosion of the metal of the workpiece may result, this action being similar to a pickling or etching action characteristic of relatively strong acid solutions on metal surfaces.

The electrolyte of this invention is readily produced by admixing the required weights of constituents into

the proper amount of water. Reagents of commercial purity will function satisfactorily. The electrolyte requires the reagents specified in solution although due to ionization they will not necessarily remain in their originally added state. Thus, as will be apparent, sodium chloride and nitric acid will provide the same ions in solution as when hydrochloric acid and sodium nitrate are originally added and the amounts of equivalent salts or acids can be regulated to provide the required solution content as defined. The complexing agent may be added as either the acid, or alkali metal or ammonium salt.

The following examples illustrate the practice of embodiments of this invention.

Example 1

An electrode made of ½ inch outside diameter stainless steel tubing was mounted vertically in apparatus arranged to feed at a downwardly rate of about 0.1 inch per minute. A flexible hose was connected to the electrode at its top and supplied with electrolyte from a tank under pressure to provide an electrolyte flow from the bottom of the electrode of about 5 gallons per minute. The electrode was connected to the negative pole of a source of electric current thereby to make it a cathode.

A plate about 4 inches thick of unalloyed titanium was placed under the electrode and connected to the positive pole of the electric current source.

An electrolyte was prepared of the following composition:

20% by weight NaCl
0.4% by weight NaF
2.8% by weight of a 30% aqueous solution of H_2O_2
Balance water

The electrolyte was fed down the bore of the electrode to flood the worksite, and the electrode was lowered into the titanium plate at a rate of 0.1 inch per minute. The electric power was turned on between the electrode as cathode and the titanium plate as anode. During the drilling operation the current flow was 500 amperes at 24 volts.

After about 40 minutes operation a hole slightly larger than ½ inch diameter had been drilled in the titanium plate. The hole was cleanly cut with sharp edges and with no pitting of the metal in the bore or around the hole. The metal in and around the hole was not discolored and was characterized by a clean metallic mat finish.

Example 2

The same workpiece procedure and apparatus was used as described in Example 1.

The electrolyte consisted if the following composition:

20% by weight NaCl
0.4% by weight NH_4F
1% by weight tartaric acid
1% by weight of a 30% aqueous solution of H_2O_2
Balance water

A clean sharp hole similar to that described in Example 1 was obtained with no evidence of discoloration of the titanium in the bore or around the hole.

Example 3

The same procedure and apparatus was employed as in Example 1 but the workpiece was a ½ inch block of unalloyed titanium.

The electrolyte consisted if the following composition:

20% by weight NaCl
0.6% by weight NaF
1.7% by weight tartaric acid
1.7% by weight of a 30% aqueous solution of H_2O_2
3% by weight HNO_3 (70%)
Balance water

A clean sharp hole was drilled in the titanium block in about 6 minutes, using 600 amperes at 24 volts. The hole was of uniform diameter and was not tapered. The corners were not badly rounded but were not as sharp as those of the holes produced in Examples 1 and 2.

Example 4

An electrode made of stainless steel tubing with a ½ inch square outlet was mounted vertically in apparatus arranged to feed downwardly at a rate of about 0.1 inch per minute. A flexible hose was connected to the electrode at its top and supplied with electrolyte from a tank under pressure to supply an electrolyte flow from the bottom of the electrode of about 1⅓ gallons per minute. The electrode was connected to the negative pole of a source of electric current thereby to make it a cathode.

A plate ¾ inch thick of unalloyed titanium was placed under the electrode and connected to the positive pole of the electric current source.

The electrolyte consisted of the following composition:

20% by weight NaCl
0.3% by weight NaF
3% by weight tartaric acid
1.3% by weight of a 30% aqueous solution of H_2O_2
5% by weight of HNO_3 (70%)
Balance water

The electrolyte was fed down the bore of the electrode to flood the worksite and the electrode was lowered into the titanium plate at a rate of about 0.1 inch per minute. The electric power was turned on between the electrode as cathode and the titanium plate as anode. During the drilling operation the current flow was about 400 amperes at 24 volts.

After about 10 minutes operation a square hole slightly larger than the ½ inch square electrode had been drilled through the titanium plate. The hole was cleanly cut with reasonably sharp edges and with no discoloration of the metal in and around the hole.

Example 5

The same workpiece and procedure was used as described in Example 4. The electrode was ¼ inch round stainless steel tube. The apparatus was arranged to feed the electrode downwardly at a rate of about ⅛ inch per minute.

The electrolyte consisted of the following composition:

20% by weight NaCl
0.4% by weight NaF
2% by weight citric acid
5% by weight of HNO_3 (70%)
Balance water

Electric current used during drilling was about 200 amperes at 24 volts. After about 6 minutes operation, a clean, sharp hole was drilled through the titanium plate and the metal in the bore and around the hole showed no discoloration. The hole was of uniform diameter and the corners were not badly rounded, but were not as sharp as those obtained in the electrolyte containing no nitric acid.

Example 6

The same procedure was used as described in Example 1. The electrode was a $1\frac{5}{16}$ inch outside diameter titanium alloy tube. The workpiece was a high nickel stainless steel alloy billet.

The electrolyte consisted of the following composition:

20% by weight NaCl
0.4% by weight NaF
2.8% by weight tartaric acid
2.8% by weight of a 30% aqueous solution of H_2O_2
Balance water

A 6 inch deep hole was drilled in the stainless steel billet during operation for 70 minutes using 500 amperes at 12 volts.

The drilled hole was cleanly cut with sharp edges and no pitting or discoloration of the metal in the bore or around the hole.

Example 7

The same procedure was used as described in Example 1. The workpiece was a 6 inch billet of A–286 high alloy steel. The electrode was a flat blade 8 inches long formed by assembling an aligned row of 1/16 inch diameter stainless steel tubes.

The electrolyte consisted of the following composition:

20% by weight NaCl
0.4% by weight NaF
2.8% by weight tartaric acid
Balance water

Using 700 amperes at 12 volts the electrode blade made a 2 inch cut in the 6 inch billet in 30 minutes. The area of cut steel showed a clean, bright, shiny surface, and there was no pitting or discoloration of the metal in or around the cut.

Potassium chloride or ammonium chloride can be substituted for the sodium chloride employed in the examples described above. These salts have similar current carrying capabilities, solubilities, and other characteristics.

Formic acid and succinic acid may be substituted for the tartaric acid and citric acid used in the examples described above. My work testing electrolytes for cutting has demonstrated that formic acid and succinic acid will produce the same general results as obtained and shown for tartaric and citric acids.

The electrolyte of this invention has specific properties and characteristics which make it useful for use in an electrolytic process for the cutting of metals. In such a process metal removal from the workpiece is accomplished by electrolytic action and not be reason of chemical solution in the electrolyte. Therefore, solutions containing high acid content or other ingredients known to produce corrosion, pickling or etching of metals cannot be substituted for the type of electrolyte herein described, nor can they be considered equivalents. An electrolyte for electrolytic cutting must function effectively to promote electrolytic action between the cathode and the workpiece, and to suppress or at least not promite dissolution of the workpiece at any other place. It will be appreciated that more of the workpiece metal surface is wet by the electrolyte than that actually being cut and removed by electrolytic action. Any pickling, etching or corrosion of the workpiece independently by the electrolyte would result in metal removal other than that desired. In cutting holes, for example, it is essential that a clean, uniform diameter hole be bored through the workpiece but if the electrolyte etches the metal then an undesirable tapered hole with rounded surface edges will result.

For this reason the electrolyte of this invention is only slightly acid, not enough to result in harmful etching of the workpiece metal. Also, for this reason the fluoride content is to be carefully controlled below a maximum concentration, and nitric acid if incorporated as an optional ingredient, must not exceed 5% by weight. However, I have found that the electrolyte composition described does promote fast, clean and effective cutting without deleterious corrosion, etching or pickling of the metal workpiece.

I claim:

1. An electrolyte, for electrolytic cutting of a workpiece of metal selected from the group consisting of reactive metals, ferrous metals, high alloy steels and super alloys, which consists essentially of:
   (a) from 5% by weight to saturation of a salt selected from the group consisting of sodium chloride, potassium chloride and ammonium chloride,
   (b) from 0.2% to 2% by weight of sodium fluoride,
   (c) from 1% to 5% by weight of an acid selected from the group consisting of tartaric acid, formic acid, citric acid, and succinic acid,
   (d) up to 4% by weight of a 30% aqueous solution of hydrogen peroxide,
   (e) up to 5% by weight of nitric acid (70%), and
   (f) balance water.

2. An electrolyte, for electrolytic cutting of a workpiece, of metal selected from the group consisting of reactive metals, ferrous metals, high alloy steels and super alloys, which consists essentially of:
   (a) from 5% by weight to saturation of a salt selected from the group consisting of sodium chloride, potassium chloride and ammonium chloride,
   (b) from 0.2% to 2% by weight of sodium fluoride,
   (c) from 1% to 5% by weight of an acid selected from the group consisting of tartaric acid, formic acid, citric acid, and succinic acid, and
   (d) balance water.

3. An electrolyte, for electrolytic cutting of a workpiece, of metal selected from the group consisting of reactive metals, ferrous metals, high alloy steels and super alloys, which consists essentially of:
   (a) from 5% by weight to saturation of a salt selected from the group consisting of sodium chloride, potassium chloride and ammonium chloride,
   (b) from 0.2% to 2% by weight of sodium fluoride,
   (c) from 1% to 5% by weight of an acid selected from the group consisting of tartaric acid, formic acid, citric acid, and succinic acid,
   (d) up to 4% by weight of a 30% aqueous solution of hydrogen peroxide, and
   (e) balance water.

4. An electrolyte, for electrolytic cutting of a workpiece, of metal selected from the group consisting of reactive metals, ferrous metals, high alloy steels and super alloys, which consists essentially of:
   (a) from 5% by weight to saturation of a salt selected from the group consisting of sodium chloride, potassium chloride and ammonium chloride,
   (b) from 0.2% to 2% by weight of sodium fluoride,
   (c) from 1% to 5% by weight of an acid selected from the group consisting of tartaric acid, formic acid, citric acid, and succinic acid,
   (d) up to 5% by weight of nitric acid (70%), and
   (e) balance water.

5. An electrolyte, for electrolytic cutting of a workpiece, of metal selected from the group consisting of reactive metals, ferrous metals, high alloy steels and super alloys, which consists essentially of:
   (a) about 20% by weight of sodium chloride,
   (b) about 0.4% by weight of sodium fluoride,
   (c) about 2.8% by weight of tartaric acid,
   (d) about 2.8% by weight of a 30% aqueous solution of hydrogen peroxide, and
   (e) balance water.

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