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ELECTROCHEMICAL MACHINING PROCESS AND ELECTROLYTE COMPOSITION OF CHLORIDES AND PHOSPHATES

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5 Claims. (Cl. 204-143)

This invention relates to electrochemical machining processes and more particularly to electrolytes for use therewith.

In recent years electrolytic machining procedures for generating shaped cavities and contoured surfaces have been developed and are generally classified into one of two basic categories, namely electrolytic grinding and electrochemical machining. An electrolytic grinding process is essentially an electrochemical deplating process which can be used on any electrically conductive material. It is generally suited to metal removal operations ordinarily performed by cut-off wheels, saws, and grinding or milling machines and uses equipment similar in appearance to conventional cutting apparatus except for the electrical accessories. About 95% of the metal removal results from electrolytic rather than mechanical action. In its simplest form electrolytic grinding is a process wherein an electric current is passed through a bath to dissolve the surface of a workpiece anode and the resultant film of insoluble salts or oxides is then scraped away by a rotating cathode grinding wheel. Electrochemical machining on the other hand relies solely on reaction product removal by means of electrochemical action and is generally characterized by a plunging action of the tool electrode and a rapid circulation of the electrolyte. The distinction between electrolytic grinding and electrochemical machining, as used herein, becomes apparent primarily in that the former process requires mechanical action for reaction product removal, i.e., a grinding wheel, whereas the latter provides for said removal by an initial dissolution of the reaction products at the workpiece-electrolyte interface, a subsequent hydroxyl precipitation of the metal ion at a point removed from the interface and a final flushing away of the precipitate resulting from the flow of electrolyte through the workpiece-to-electrode gap.

While aqueous solutions of individual inorganic salts, such as nitrates and nitrites, have been used as electrolytes in electrochemical machining processes, none has offered any significant advantage over the now well accepted aqueous sodium chloride solutions most commonly used today. However, regardless of the salt or salt combinations used heretofore, an inherent problem in electrochemical machining processes is that of overcut. This is the uncontrolled anodic dissolution of the workpiece in unwanted areas resulting in undesirable tapering of holes, rounding of edges, and the like. Such anodic dissolution can occur even in areas which are fairly well removed from the cathode. This overcut or cutting in low current density areas which are bathed in the electrolyte but substantially removed from the cathode has been substantially reduced in the prior art by the use of costly and time-consuming masking operations which isolate the areas to be machined by protecting the surrounding areas from the erosive effect of the electrolyte. These masking operations are frequently quite involved and require a high degree of skill to insure a satisfactory product. Likewise, additional steps subsequent to the machining steps are required to strip the workpieces of the masks. Additionally, the prior art has attempted to reduce overcut by designing special purpose electrodes and machines to meet individual and specialized machining requirements. By my invention, I have

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at least simplified, and in most cases, actually eliminated these prior art requirements.

It is therefore an object of this invention to produce an accurately electrochemically machined article having desirable machined surfaces.

It is an object of this invention to eliminate the need for premasking of the workpiece in order to effect a sharply contoured machining by utilizing a self-masking electrolyte.

It is an object of this invention to produce the desired machining contour by an electrochemical process utilizing an electrolyte comprising a solution of chlorides, nitrates and phosphates in a balanced relationship within fixed limits with the particular concentration configuration being variably dependent upon the composition of the workpiece.

These and other objects and benefits will become apparent from the following description of specific embodiments encompassed within the scope of my invention.

I have discovered electrochemical machining processes can be improved by utilizing electrolytes which form electrochemical erosion inhibiting films over the surfaces to be machined. The films are subsequently selectively decomposed by the application of high current densities to the areas that are to be machined, thereby destroying the film in those areas and permitting continuous cutting thereat. The surrounding areas which are subjected to lower current densities and stray currents retain the film and hence are not machined.

I have discovered that products displaying smooth surfaces and sharp contoured machinings, with minimum overcut, can be produced by ECM processes using an electrolyte comprising chlorides, nitrates and phosphates wherein the concentration of the nitrate varies from 0.1 to 0.45 equivalent of nitrate per equivalent of chloride and the concentration of the phosphate varies from small but effective amount up to 0.10 equivalent of phosphate per equivalent of chloride when the electrolyte is used within a temperature range of from 70° F. to 160° F. The lower limit is a variable depending on the composition of the workpiece but is generally at least about 0.002 equivalent of phosphate per equivalent of chloride. The ratio of nitrate ions to chloride ions controls the relative metal removal rates of the grains and grain boundaries of various alloys as disclosed in copending patent application A 4,187. The phosphate ion inhibits the formation of micro-pits, levels the relative metal removal rates of the chloride and nitrate ions, and restricts the electrochemical action to relatively high current density areas. These actions of the phosphate ions are due to the formation of dielectric metal phosphate films on the alloy surface. The strength of this dielectric film on a given metal is dependent on the phosphate ion concentration, the temperature, and the extent of the surface irregularities of the workpiece. A film of given dielectric strength requires a related minimum current density to break it down.

This process is concerned with the elimination of the last trace of passivation in the area to be machined. The chloride ion activates the metal surface. The phosphate ion passivates the metal surface. Necessarily, therefore, it is the balancing of the respective ion activities and hence the ratio of the concentration of the respective ions that is more important than the individual concentration of either. The proper balance insures the formation of a film which will break down as desired under given operating current densities. As the current density varies so must the ion ratio to insure a film formation most susceptible to complete breakdown at that particular current density. Too low a phosphate concentration would yield a film which would break down in the unwanted low current density areas. Too high a concentration would produce a film which would not break

down under practical operating current densities. Since my invention resides in use of a dielectric film producing ion, especially phosphate, and its relation to the chloride ions in solution, the limits and ratios were established in the absence of nitrate ions. The nitrate ions were later added to the electrolyte to equalize the metal removal rates of the grains and grain boundaries as disclosed in aforementioned copending patent application A 4,187. The nitrate addition herein forms no part of the incident invention. The lower limit of the phosphate ion concentration was established by noting the point where the first improvement in machining detail and micropit elimination became evident. Tests were conducted on SAE 903 zinc alloy utilizing an electrolyte comprising 16 ounces per gallon of sodium chloride with 2 and 4 grams per gallon of tripotassium phosphate, respectively, at a current density of 30 amperes per square inch, an electrolyte temperature of 80° F., an initial electrode gap of 0.015 inch, an electrolyte pressure of 20 pounds per square inch, and an electrolyte flow rate of 30 feet per second. The electrolyte having 2 grams of phosphate per gallon yielded a product displaying a gray granular surface, whereas the electrolyte having 4 grams of phosphate produced a product displaying a silvery granular surface. Upon investigation it was determined that the sole difference between the two machinings was the presence of micropits in the gray granular surface produced from the electrolyte utilizing but 2 grams per gallon of tripotassium phosphate. Similar tests were conducted on SAE 1010 and 1020 cold rolled steels under the same operating conditions, and it was discovered that satisfactory results could be obtained with the steel at phosphate ion concentrations less than the minimum concentration required to electrochemically machine the zinc samples. In fact it was noted that for the same operating conditions the lower limit of phosphate ion concentration required for SAE 903 zinc approximates the upper practical limit of that required for cold rolled steel.

Maximum metal removal efficiency was noted in the range of 120° F. plus or minus 10° F. Best surface conditions were produced between 100° F. and 120° F. The minimum current density at which it is practical to operate these electrolytes is 10 amperes per square inch and the maximum is limited only by the electrolyte flow rates and the rate at which heat can be dissipated by the particular equipment being used. In fact, I have found that though for most practical ECM applications, current densities ranging from 100 to 2,000 amperes per square inch are adequate, current densities as high as 4,000 amperes per square inch are possible.

It is significant that it is the concentration ratio of the phosphate ion to the chloride ion that is important here. The means whereby the phosphate ion is introduced into the solution is only of secondary import, having a bearing only on factors other than the production of the subject dielectric film i.e., salt concentration, solubility, etc. Hence I know, for example, that the pyrophosphate radical can be substituted for the phosphate on the basis of ½ mole pyrophosphate per mole of phosphate which equates to a practical operating range of 0.0013 to 0.0661 equivalent of pyrophosphate per equivalent of chloride. Likewise dibasic phosphate salts or any other salt which will yield the phosphate ion within the ranges of my invention can be used merely by adjusting the concentration of the salt additive as a function of its ability to generate phosphate ion. In selecting any such salt, cognizance should be taken not only of the salt's solubility but also any hydrolysis reactions incident to its dissolution. Likewise the corresponding acids of the respective salts of this invention may be substituted.

The concentration of the chloride ion is not in and of itself critical but is rather determined by the practicality of usage of one concentration over another. I have found, for example, that solutions containing chloride concentrations varying from dilute to saturation

are operative but have concluded that as a practical matter there are no benefits to be derived by operating at concentrations below 16 ounces per gallon of sodium chloride, as solution conductivity and metal removal rates are affected. As a general rule, the lighter alkali metal (i.e. Li, Na and K) salts of all the subject anions are preferred because they produce relatively neutral pH's, do not plate out or have a deleterious effect upon the cathode, and represent a source of inexpensive material.

It has been also noted that in addition to limiting overcut, some improvement in the surface finish produced with a simple sodium chloride electrolyte has been obtained by adding solely alkali metal phosphates to the chloride electrolyte within the limits defined above.

I have found that the phosphate ion will produce the same effect on other metals as on zinc. The concentration required, however, will vary depending on the nature of the metal to be machined. Generally, in a simple chloride electrolyte, for example, only ⅓ of the phosphate ion concentration used on zinc is required to effect the same inhibition on cold rolled steel.

The following are specific examples of my invention:

Example 1

An aqueous bath comprising 16 ounces per gallon of sodium chloride, 4 ounces per gallon of potassium nitrate and 10 grams per gallon of tripotassium phosphate was used for two minutes to machine a sample of SAE 903 alloy at a current density of 30 amperes per square inch and a bath temperature of 80° F. The electrolyte was forced through the workpiece-to-electrode gap at a rate of 30 feet per second under a pressure of 20 pounds per square inch. A metal removal rate of 0.005 inch per minute was noted and the finished sample exhibited a very smooth but slightly preferentially removed grain boundary while the machining exhibited sharp contours with minimum overcut.

Example 2

An aqueous bath comprising 16 ounces per gallon of sodium chloride, 4 ounces per gallon of potassium nitrate and 8 grams per gallon of tripotassium phosphate was used for two minutes to machine samples of SAE 903 alloy at a current density of 30 amperes per square inch and a bath temperature of 100° F. The electrolyte was forced through the workpiece-to-electrode gap at a flow rate of 30 feet per second while maintained under a pressure of 20 pounds per square inch which gap was initially maintained at 0.035 inch. A metal removal rate of 0.007 inch per minute was noted and the finished sample exhibited a very smooth and bright surface. This same bath was used under similar conditions varying only the temperature from 80° F. to 140° F. While generally good results were obtained at all the temperatures tested, the best results occurred at 100° F.

Example 3

An aqueous bath comprising 16 ounces per gallon of sodium chloride, 4 ounces per gallon of potassium nitrate and 14 grams per gallon of tripotassium phosphate was used for 40 seconds to machine samples of an SAE 903 alloy at a current density of 90 amperes per square inch, and an electrolyte temperature of 120° F. The electrolyte was forced through the workpiece-to-electrode gap at a flow rate of 30 feet per second while maintained under a pressure of 20 pounds per square inch, which gap was initially maintained at 0.015 inch. A metal removal rate of 0.020 inch per minute was noted and the finished sample exhibited a smooth and bright surface. The same bath was used varying the temperatures from 80° F. to 140° F. and the current density from 30 to 90 ASI. Generally, speaking, grain boundary etching increased with temperature increase and more uniform erosion was obtained with increased current densities.

Example 4

An aqueous bath comprising 16 ounces per gallon of sodium chloride, 4 ounces per gallon of potassium nitrate and 25 grams per gallon of tripotassium phosphate was used for 40 seconds to machine samples of an SAE 903 alloy at a current density of 90 amperes per square inch, and a temperature of 110° F. The electrolyte was forced through the workpiece-to-electrode gap at a flow rate of 30 feet per second while maintained under a pressure of 20 pounds per square inch, which gap was initially maintained at 0.015 inch. A metal removal rate of 0.005 inch per minute was noted and the finished sample exhibited a smooth, bright surface, while the machining exhibited sharp contours and minimum overcut.

Example 5

An aqueous bath comprising 16 ounces per gallon of sodium chloride, and 4.34 grams per gallon of disodium phosphate was used for 16 seconds to machine samples of an SAE 1020 cold rolled steel at an initial current density of 1000 amperes per square inch, and a temperature of 115° F. The electrolyte was forced through the workpiece-to-electrode gap at a flow rate of approximately 100 feet per second while maintained under an initial pressure of 180 pounds per square inch which gap was initially established at 0.005 inch. A metal removal rate of 0.005 inch per minute was noted and the finished sample exhibited a smooth, deburred finish while the machining exhibited sharp contours and minimum overcut. Similar tests were conducted with SAE 1010 steel with equally good results.

Though I have disclosed the use of phosphates as agents for the formation of films which will selectively decompose under high current densities thus selectively applied, it is to be understood that others may be adopted and that the scope of my invention is not limited except as by the appended claims.

I claim:

1. An aqueous electrochemical machining electrolyte consisting essentially of alkali metal chlorides, phosphates, and nitrates wherein the concentration of said phosphate ion is from 0.002 to 0.10 equivalent of phosphate ion per equivalent chloride ion and the concentration of said nitrate ion is from 0.1 to 0.45 equivalent of nitrate ion per equivalent of chloride ion.
2. A process for electrochemically machining a metal comprising the steps of establishing said metal as the anode in an electrochemical cell, orienting an electrode adjacent to but closely spaced from said metal to form a gap therebetween, flowing through said gap an aqueous electrolyte consisting essentially of a mixture of alkali metal chlorides and phosphates, wherein the concentration of said phosphate ion is from 0.002 to 0.10 equivalent of phosphate ion per equivalent of chloride ion which form an electrochemical erosion inhibiting film on the surface of the metal which film decomposes at high current densities, and passing current through said metal, electrolyte and electrode to decompose said film in selected areas whereby electrochemical machining can continue in said areas.
3. A process in accordance with claim 4 wherein said electrolyte also contains alkali metal nitrates, wherein said nitrate ion concentration is from 0.1 to 0.45 equivalent of nitrate ion per equivalent of chloride ion.
4. A process in accordance with claim 4 wherein the alkali metal phosphate is dibasic.
5. A process in accordance with claim 3 wherein said alkali metal phosphate is dibasic.

References Cited

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ROBERT K. MIHALEK, *Primary Examiner*.

U.S. DEPARTMENT OF COMMERCE

PATENT OFFICE

Washington, D.C. 20231

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

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It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, lines 24 and 28, the claim reference numeral "4", each occurrence, should read -- 2 --.

Signed and sealed this 10th day of February 1970.

(SEAL)

Attest:

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