Oct. 31, 1944. R. A. EHRHARDT 2,361,680

METHOD OF REDUCING EDGE LEAKAGE IN METAL OXIDE-METAL RECTIFIERS

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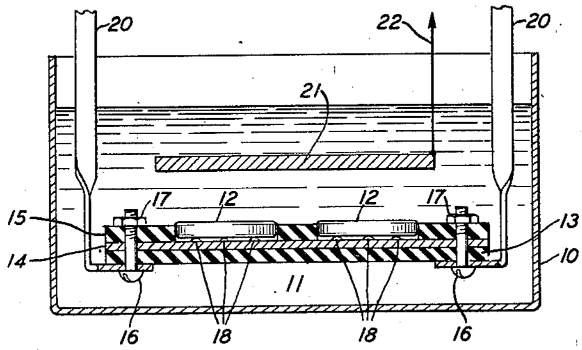
FIG. 1



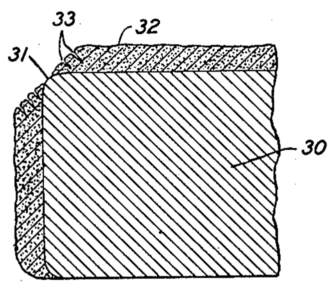


FIG. 2

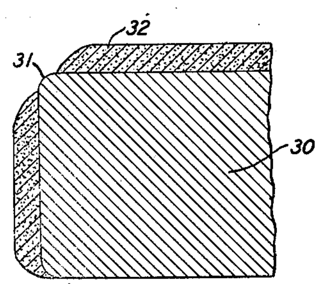


FIG. 3

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METHOD OF REDUCING EDGE LEAKAGE IN METAL OXIDE-METAL RECTIFIERS

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1 Claim. (Cl. 204—141)

This invention relates to metal oxide-metal rectifiers and, more particularly, to cuprous oxide-copper rectifiers.

In the making of metal oxide-metal rectifiers, it has been found that fissures and other imperfections in the oxide adjacent to the edges of the rectifier unit, have formed paths of relatively low resistance to current flowing in the normally high resistance direction. This unwanted flow of current is one of the factors making up what is known as edge leakage. Various methods have been employed for reducing this leakage. Among these are mechanical abrasion to remove the loose or semiloose particles of metal oxide from the edges of the unit. The edges of rectifier units have also been cleaned by immersing them for short times in various solutions that attack the oxide, e. g., various acids. In carrying out the various methods previously employed, it has been necessary to exercise considerable care to avoid damage to the rectifier unit. In the acid dip method of cleaning cuprous oxide-copper rectifiers, there is a considerable tendency for copper to redeposit from the solution during rinsing. Dissolution of the copper oxide takes copper into the solution and upon dilution by rinsing with water, the high copper ion concentration coupled with the potential difference between copper and copper oxide cause electrolytic redeposition of the copper. That portion of the redeposited copper which adheres to the edges of the unit forms low resistance paths across the rectifying junction thereby increasing edge leakage.

An object of this invention is to clean leakage paths from the edges of metal oxide-metal rectifier units without injury to said units.

One feature of this invention resides in making the rectifier unit the anode in an electrolytic solution and passing current therethrough in the high resistance direction.

The solution employed is one in which copper and copper oxide, or the other materials from which the rectifiers are made, are relatively insoluble unless current is flowing.

Another feature of this invention resides in making the current density sufficiently high to cause polarization on the copper or other metal, which inhibits the attack of the electrolytic solution thereon.

A further feature of the invention resides in employing an electrolyte having an anion with high polarization properties to minimize dissolution of the metal portion of the rectifier unit.

Another feature also related to the solution involves selection of a cation producing an electrolyte having a relatively low acidity to inhibit redeposition of metal on the cleaned unit. Where cuprous oxide-copper units are treated, the acidity is chosen so that the precipitation tendency is reduced and the copper which may be precipitated is in combination as the hydroxide thereof.

Another feature of the invention depends upon the fact that the current concentrates in the leakage paths and dissolves the oxide therearound. When all leakage paths are removed, the rectifier action cuts down the current and thereby the rate of solution. The action then proceeds so slowly that if the unit is removed within a reasonable time thereafter, no undue dissolving of the rectifier body takes place.

Other objects and features of this invention will be more clearly and fully understood from the following description of illustrative embodiments thereof taken in connection with the appended drawing, in which:

Fig. 1 is a sectional view of an illustrative embodiment of apparatus suitable for carrying out the invention; and

Figs. 2 and 3 are fractional sections of a rectifier unit with portions exaggerated to illustrate edge conditions before and after the treatment according to this invention.

Referring to the drawing and particularly to Fig. 1, 10 is a tank or other suitable receptacle containing an electrolyte. Suspended in the tank 10 is a rack 11 for supporting a plurality of rectifier units 12 in the electrolyte. The rack 11 may comprise a back plate 13 of insulating material, such as hard rubber or the like; a plate 14 of conducting material and a front plate 15 of similar material to plate 13. The plate 15 is provided with a plurality of orifices for the reception of the units 12. The plates 13, 14 and 15 may be held together by fastening means, such as bolts 16 and nuts 17. The rack may be supported by a pair of hangers or supports 20. The hangers 20 may be secured to the rack by means of the fastening means 16 and 17. The bolts 16 electrically interconnect the metallic plate 14 and hangers 20 so that said hangers may serve as connecting means to the current source. The plate 14 may be provided with a plurality of small raised portions 18 to insure good electrical contact to the back of the unit 12.

A cathode member 21 may be suspended in spaced relation to rack 11 by any suitable means, for example, like hangers 20. The connection from the cathode to the current source is represented by 22. The cathode 21 may be of any suitable conducting material. The use of a copper cathode has been found advantageous when treating cuprous oxide-copper units.

The electrolyte employed should be one in which both the metal and the metal-oxide are relatively insoluble except when current is flowing therein. The anion of the electrolyte should be chosen for its polarization properties. The flow of current then quickly makes the metal surfaces relatively passive, so that the oxide is dissolved at a much higher rate than the metal. This may be accomplished at a relatively low current density in the order of 0.125 ampere per square inch of rectifier surface with a suitable electrolyte. With any given electrolytic solution, the current density should be high enough to cause rapid polarization. During the electrolytic dissolution of the metal oxide, as in the case of the acid dip, metal is taken into the solution. To avoid redeposition of the metal after the current flow is discontinued and during rinsing, the cation thereof should be selected for low acidity. Electrolytes in which the cleaning can be satisfactorily carried out are phosphoric acid and various sulphates such as ammonium and sodium sulphate. With phosphoric acid there is some metal redeposited, which must be removed, for example, by dipping in concentrated nitric acid. The sulphates are sufficiently low as to acidity, to substantially prevent any redeposition of metal. For example, where the metal is copper and the solution ammonium sulphate, there is no redeposition of copper. This is due to two factors: (1) the copper is, to a considerable extent, precipitated in the bath as the hydroxide which greatly lowers the copper ion concentration; (2) the low acidity of the solution inhibits precipitation of the remaining copper ions.

With the racked units and cathode means positioned in the bath, current is applied to the terminals. It is noted that the connection to the unit 12 is to the back or copper portion thereof. Due to the rectifying action of the unit a high resistance is presented to the passage of current through the oxide except where there are leakage paths or exposed copper. The current density is kept sufficiently high to quickly render the copper relatively passive. The rate of dissolution of copper then is much lower than that of oxide. As the copper oxide is dissolved around the paths more and more current flows through the copper and the dissolving action slows down. The unit should, however, be removed from the solution before enough copper has been dissolved to undercut the oxide layer. Since the rate of dissolution of copper is very slow, this time is, however, not critical.

Since the removal of the leakage paths raises the over-all resistance of the unit, this change in characteristic may be employed to indicate when the action has reached completion. This could be done by measuring the voltage drop across the unit. As this technique might not be sufficiently accurate if applied to a rack full of units, modification of the method may be used when cleaning many units on a production basis. One way of doing this is to remove the treated units from the rack and test each one individually, returning those not sufficiently clean for further processing. The best practical method is probably to work out the conditions of treatment by experiment to obtain satisfactory average conditions. Since the dissolution of the metal is inhibited by polarization and that of the oxide greatly reduced by removal of the fissured material, processing for a sufficient time to clean the worst unit should result in suitable characteristics for all units.

The edges of the unit must be properly "chipped" before processing. Ordinarily, this is taken care of during the oxidizing process. Internal stresses on the edge of the unit cause the oxide to chip off fairly uniformly upon quenching. As is illustrated in Fig. 2, a properly chipped unit has a small area of the copper 30 exposed as at 31. The portion of the oxide 32 adjacent the edge has small cracks or fissures 33 that form the leakage paths.

Fig. 3 illustrates the condition of the edge of the unit after the completion of the process of this invention. The copper at 31 is smoothed and rounded off and the oxide around the fissures 33 has been removed. This leaves a clean-cut edge with no paths of relatively low resistance in the high resistance direction. In other words, leakage paths have been removed.

Although the invention has been disclosed with reference to a specific illustrative embodiment thereof, it will be understood that it is not restricted thereto but is limited in scope by the appended claim only.

What is claimed is:

The method of cleaning from the previously chipped edges of copper oxide-copper rectifier units that portion of the oxide containing low resistance paths, that comprises placing the units in a solution of sodium sulphate, connecting the copper part of the units to the positive pole of a current source, passing current through the units in the high resistance direction to electrolytically dissolve that portion of the oxide adjacent the low resistance paths, maintaining a current density sufficiently high to insure substantial passivity of the copper by polarization, and removing the units from the solution when the low resistance paths have been eliminated.

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