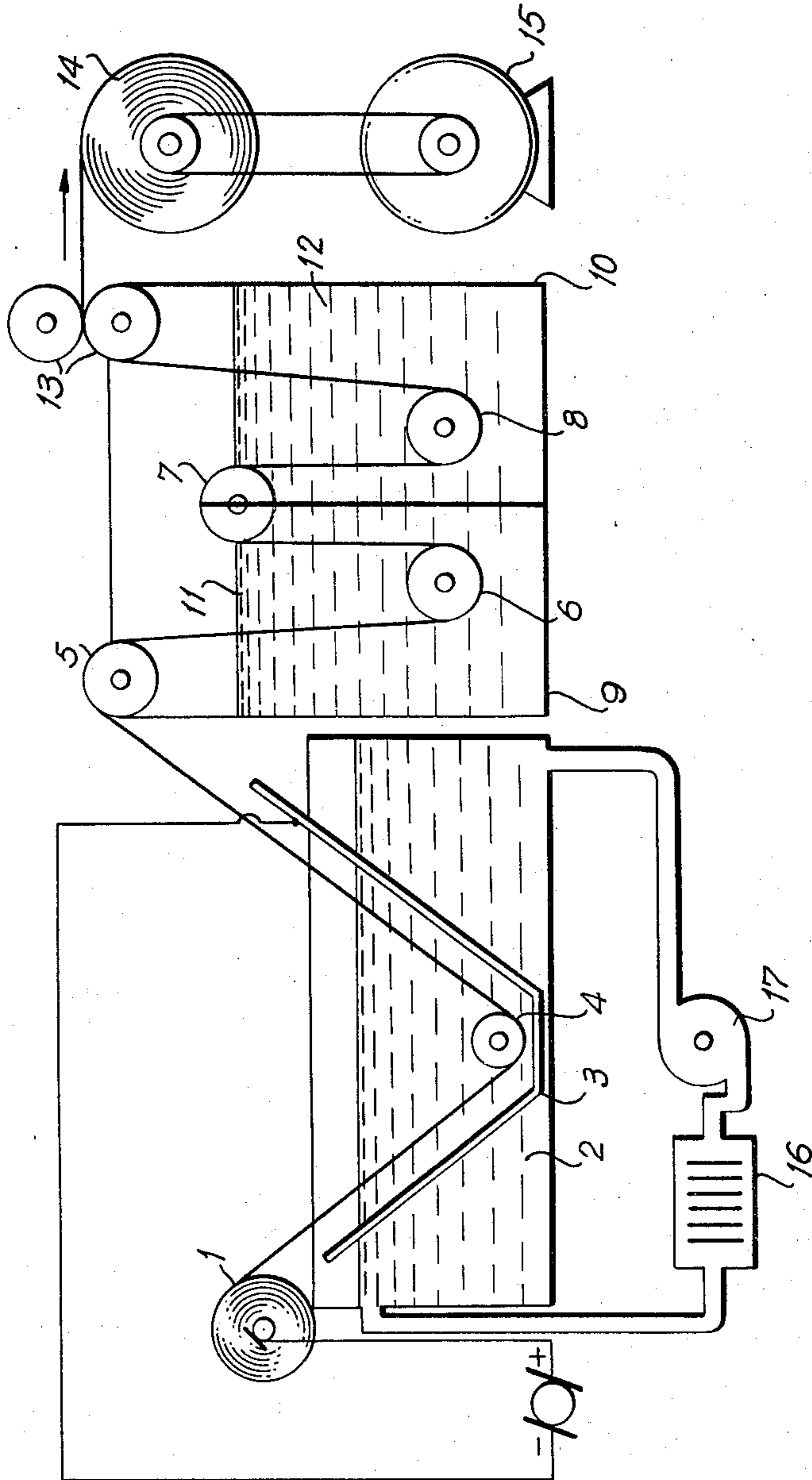


Nov. 14, 1967

S. RUBEN  
PROCESS FOR PRODUCING MICROPERFORATED  
STAINLESS STEEL SHEETS  
Filed Jan. 11, 1967

3,352,769



INVENTOR.  
SAMUEL RUBEN

3,352,769

**PROCESS FOR PRODUCING MICROPERFORATED STAINLESS STEEL SHEETS**

Samuel Ruben, 52 Seacord Road,  
New Rochelle, N.Y. 10804

Filed Jan. 11, 1967, Ser. No. 615,288  
13 Claims. (Cl. 204-143)

**ABSTRACT OF THE DISCLOSURE**

The invention is a process for producing microperforated stainless steel sheets. It comprises connecting a sheet of stainless steel as the anode in an electrolytic cell containing a non-polarizing electrolyte and discharging direct current through the cell to produce a multiplicity of light transmitting microperforations through the sheet, the perforations being due primarily to electrochemical action.

This application is a continuation-in-part of my co-pending applications: Ser. No. 422,005 filed Dec. 29, 1964, which was a continuation-in-part of my application Ser. No. 345,071 filed Feb. 17, 1964; Ser. No. 472,617 filed July 16, 1965, which was a continuation-in-part of application Ser. No. 304,667 filed Aug. 26, 1963; Ser. No. 556,921 filed June 13, 1966, and Ser. No. 585,054 filed Oct. 7, 1966, all of which have become abandoned.

This invention relates to a process for producing microperforated stainless steel sheets and to products made therefrom such as filters and diaphragms. In a preferred form, microperforated stainless steel strip is produced in a continuous operation.

An object of the invention is to provide a simple, inexpensive process for producing microperforated stainless steel.

A further object is to provide a microperforated stainless steel sheet adaptable for use as filter, diaphragm and separator elements.

Other objects will be apparent from the disclosure and the drawing which illustrates the process in schematic form.

Various means have previously been used for producing metal plate filters, for instance, by pressing and sintering metal powder to produce a porous mass. In the present invention, relatively thin non-porous stainless steel sheet produced from cast and rolled alloy is utilized as the starting material.

The invention comprises connecting a sheet of stainless steel as the anode in an electrolytic cell containing a non-polarizing electrolyte and discharging direct current through the cell to produce a multiplicity of light transmitting microperforations through the sheet, the perforations being primarily due to electrochemical action.

A method is provided for uniformly perforating thin stainless steel sheet in a continuous process whereby microperforations are obtained at the grain boundary of the metal crystal structure with selective anodic dissolution at these points and with negligible anode dissolution of the face of the crystals so that the thickness of the sheet remains substantially the same. The microperforations are substantially uniformly distributed throughout the sheet and vary with the composition of the alloy.

The process utilizes stainless steels which are formed by the addition of chromium to iron, with a minute quantity of carbon and containing a lesser amount of nickel, such as 8%, as well as stainless steels composed essentially of iron and chromium without the addition of nickel, the chromium usually being present in the order of 12% or more. Both types of stainless steel may contain minor additions of other metals. All of the various types and grades

of stainless steel, as commonly known, including the #200, #300, #400 and #500 series may be utilized. Stainless steels generally contain a minimum of approximately 11½% chromium. An essential factor for producing uniform microporosity is the iron content, as without iron, anodic grain boundary perforations would not occur, these microperforations being obtained without substantially affecting either the thickness or the smooth light reflecting surface of the stainless steel sheet.

While hydrochloric acid of a concentration in the order of 2% and not exceeding 7% is the preferred electrolyte, other non-polarizing electrolytes may be employed, for example, hydrobromic acid and halogen salts which when dissolved, hydrolyze to an acidic electrolyte, such as the chlorides and bromides of iron, nickel, cobalt or manganese. The alkali and alkaline earth metal chloride salts and ammonium chloride salts will not provide anodic perforation of the chromium nickel stainless steels, such as the 300 series, but will uniformly perforate the nickel free types, such as the 400 series. Unpredictably, I have also found that the bromides of the alkaline earth metals will anodically perforate both types of stainless steel.

When chromium nickel stainless steel, such as No. 302, containing approximately 8% nickel is made the anode in an electrolyte of an alkali or alkaline earth metal halogen salt, such as the chlorides of Li, Na, K, Sr, Be, Mg, Ca and Ba, or the ammonium halogen salt or sea water, only a slight surface etch is noted with an occasional large pit. These electrolytes do not appear suitable for use in the microperforating process. However, when nickel-free stainless steel such as #430 is connected as the anode in the same type electrolyte, substantially uniform microperforations are obtained.

I have also found that bromides of the alkaline earth metals, for instance, the bromides of Ca, Mg, Sr and Ba, as well as low concentrations of hydrobromic acid such as 2% will provide perforation of both nickel and nickel-free stainless steels. Apparently the unexpected result with the bromide electrolytes is due to the di-valent nature of the basic ion. Current density and time are generally the same for the bromide electrolytes as the chloride electrolytes.

For operation over long periods it is desirable to add an adequate amount of either hydrochloric acid or hydrobromic acid to dissolve the oxides formed during processing and particularly to prevent the rise in pH of the electrolyte. The salt solutions may in some instances be made initially acidic through the addition of HCl or HBr to maintain a minimum polarization or anodic voltage drop.

A basic factor for the operation of this process is the non-polarizing character of the electrolytes. The intergranular precipitates are dissolved into the electrolyte and the formation of a passive oxide surface, usually associated with anodic effect with stainless steel, is avoided.

When hydrochloric acid is used as the electrolyte, the concentrations of the acid are held to definite limits. For instance, if No. 430 stainless steel is processed at a temperature of 25° C., the concentration of the hydrochloric acid is critical and must be kept below 4.7%. My tests show that a concentration of 4.65% will not allow perforation of the sheet while a concentration of 4.6% hydrochloric acid at a current density of 6 amperes for 4 minutes on a 12 inch square area provides a uniform perforation.

The #400 series of stainless steels are substantially nickel free, grade #430 having an approximate of .12% carbon, 1% manganese, 1% silicon, 14% to 18% chromium and the remainder iron. The #300 series of stainless steels contain nickel. For example, type 304 contains approximately 8% nickel and approximately 18% chromium, the balance being substantially iron. At 25° C., with stainless

steel compositions of these types, the concentration of hydrochloric acid in the solution must not exceed 7%.

It should be understood that when hydrochloric acid is used, the electrolyte is only initially pure hydrochloric acid. When the anodic treatment of the stainless steel commences, anodic dissolution of the precipitated chromium-iron compounds at the grain boundaries takes place and the color of the electrolyte changes from a clear solution to a green solution containing chromium and iron chlorides, with the chromium chloride content apparently being higher than that of the iron chloride content. The amount of chromium or iron chlorides produced depends upon the length of time the solution is used and the reduction of the initial hydrochloric acid content can be noted by the rise in pH during processing. To maintain uniformity over a period of time during continuous operation of the process, hydrochloric acid is added when required to keep the pH at the desired value. The preferred initial electrolyte is hydrochloric acid of a concentration of approximately 1% to 2% and as mentioned above, this may be maintained by the addition of small amounts of hydrochloric acid during continuous processing. The concentration should desirably not substantially exceed 2%.

Perforations will not occur when stainless steel sheet is immersed in hydrochloric acid without the application of current; and with concentrations of 4.65% or less, there is negligible effect on the thickness and weight of the sheet, even after a long period of immersion. With the higher concentrations of hydrochloric acid with or without the application of current, etching and dissolving of the surface of the entire sheet takes place with reduction in thickness and weight.

When ferric chloride is employed as the electrolyte, the concentration may vary between 5% to 50%, preferably between 10% and 20%. The pH of the ferric chloride electrolyte is important—the lower the pH the less current density and time required for a given degree of porosity. A typical solution having a concentration of 20%  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  has a pH of about 1.1. The concentrations of the other halogen salt electrolytes may be of the same order as that of the ferric chloride electrolytes.

While the fluorides are more expensive and more difficult to handle, some of the soluble fluorides, such as  $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ , may be used.

Referring to the drawing, the roll of .0025 inch thick No. 430 stainless steel 1 constituting the anode, is passed through a HCl electrolyte 2 via plastic roller 4, the foil being kept under tension and passing through the electrolyte at a speed determined by the degree of porosity desired. For example, a 6" x 6" wide area would be immersed in the electrolyte for 4 minutes with an applied current of 18 amperes or 288 ampere minutes per square foot. The cathode 3 is a strip of titanium material which extends over the area being treated. Titanium exhibits a special superiority for this use. It is inert in the electrolyte, possesses adequate conductivity and is capable of continuous use without chemical or electro-chemical effect. After passing through the electrolyte, the stainless steel foil passes into two wash tanks 9 and 10 via rollers 5, 6, 7 and 8, the water 11 and 12 in the tanks eliminating any retained electrolyte. A supersonic transducer may be utilized to provide additional cleaning action and to prevent undesirable electrode polarization or anodic cleaning may also be employed. The foil is then passed through rollers 13 and wound into coil 14, motor 15 serving as the driving means. Filter 16 and pump 17 insure a continually circulating filtered electrolyte. If desirable, the speed and current can be photoelectrically controlled by measuring the light transmission through the perforated foil after washing and the degree of perforation can thereby be controlled within close limits. The stainless steel sheet so processed retains a smooth light reflecting surface and its mechanical strength.

In order to maintain uniformity in a continuous proc-

ess, it is necessary, as mentioned above, to replace the halogen content which can be done by adding an acid component; for instance, with chlorides it is desirable to add hydrochloric acid to prevent the electrolyte pH from increasing too much and with the bromides, hydrobromic acid. The use of sea water or other natural brine water can provide a continuous supply of electrolyte without the necessity of adding an acid component.

It is desirable to control the temperature of the electrolyte so that it does not rise much above 30° C., in order that the perforations produced in the stainless steel will be uniformly controlled by the current density and time and due only to the electrochemical anodic action. Control of the temperature will produce a duplicatable porosity with holes of uniform size and shape and with adequate heat dissipation area of the electrolyte container or by water cooling, this temperature limit can be maintained. By control of the density applied to the electrode and the speed of the stainless steel strip through the electrolyte, variations in the porosity can be effected through a wide range.

The nature of the current is of considerable importance, substantially continuous unidirectional current being highly desirable. For example, if alternating current is applied at the preferred current discharge of 72 amperes per square foot, there is no perforation above a negligible amount—less than 0.5%—and this could be ascribed to solution effect. If half wave rectified direct current is applied at 72 amperes per square foot, a photometer reading of 8 is obtained, compared with a reading of 55 where full wave rectified current is utilized. When continuous direct current from a battery is applied, a comparative light transmission value of 64 is obtained. With a three phase rectified full wave current of the same density, a comparative light transmission of 62 is obtained.

The voltage required for operation of the continuous process will vary with temperature and electrolyte concentration, size, spacing and area of the electrodes. In a continuous process, with current density of about 72 amperes per square foot, it may be in the order of 12 volts DC.

The concentration of electrolyte depends to some extent upon the desired size of the perforations. For most applications I have found an electrolyte concentration of 2% with HCl, or HBr, 4% CaBr and 10% with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , to be satisfactory. The thickness of the stainless steel sheet should preferably be not greater than .005" and not thinner than .0005", a preferred range being from .002" to .003".

The number of perforations may vary considerably with current, time and alloy composition. In general, they may average in the order of 10 to 40 microns and approximately 15,000 per square inch. The size and number of perforations cited are those measurable on microphotographs against a standard scale, but the figures given may be less than the actual number because the smaller perforations will not pass enough light for the film.

The stainless steel, prior to being subjected to the micro-perforating process, may be sand blasted so as to produce a uniform mechanical etch resulting from blasting out by sand impact of a certain amount of steel. Where a smooth, light reflecting surface is not essential, the sand blasting allows a more uniform perforation pattern.

For some applications it is desirable to provide micro-perforations of submicron size, particularly where the element is used for dialysis. In such cases the microperforated stainless steel produced according to the process above described may be impregnated with a microporous membrane producing material. The choice of the impregnating material depends upon the application—for example, whether the final product is to be used for filtering out micron or submicron size particles, whether it is to resist hydraulic flow and heat, yet be capable of the diffusion of gasses or ions therethrough.

For most applications this involves the impregnation

of the grain boundary microperforations with a liquid of a compound which when dry and solid can be leached out—that is to say, the liquid compound would have a soluble component. Examples of suitable materials include resins, such as polystyrene, co-polymers of polyvinyl chloride and acrylonitrile, silicone lacquers, polyvinyl alcohol or its derivatives, with a leachable plasticizer and made insoluble by formaldehyde, ethyl and methyl celluloses or cellulose esters, such as a 10% solution of cellulose acetate in acetone, rendered insoluble, gelatin rendered insoluble with soluble chromates, etc. One type of water leachable microporous material is a 3% polyethylene with 15% polyethylene oxide, the polyethylene oxide being extracted with water.

For applications requiring low hydraulic passage but high gas diffusion, I use stainless steel sheets of 1 mil thickness which have been microperforated, washed and dried and subsequently impregnated with a silicone solution which when dry leaves a thin membrane of silicone on a strong base, thus permitting handling with ease for dialysis application. A suitable material is one derived from spraying a silicone solution commercially known as "Glaskote" or Ucarsil R-104 which contains 4.7% silicone solids. The thin silicone membranes can be free from holes and still be permeable to gases as well as impermeable to low pressure hydraulic flow of salt solutions.

The porous stainless steel sheet may also be impregnated with an inorganic material such as an aqueous solution of sodium silicate in which the sheet is dipped. When dry the sheet is treated with the acid solution, such as sulfur acid, which leaches out the sodium components and leaves a microporous insoluble silicate membrane. Thin fluorocarbon coatings may also be employed to form permeable membranes in the grain boundary pores.

The microperforated stainless steel sheets of this invention may be used in many applications where a strong, oxidation-resistant filter or microporous member is desired. For example, as a gasoline, oil, blood or other liquid filter, an air filter in air conditioners, a lens or hood in place of dark glasses for welding goggles, a base electrode for fuel cells, a microporous separator for electrochemical cells, gas generators and electrode reactive cells, etc.

I claim:

1. An electrically controlled process for producing microperforated stainless steel which comprises connecting a sheet of stainless steel having a thickness between approximately .0005" and .005", containing intergranular iron chromium precipitates and containing as essential elements a preponderance of iron and a lesser but significant amount of chromium as the anode in an electrolytic cell having a non-polarizing electrolyte and a cathode and discharging direct current through said cell so as to anodically dissolve intergranular iron chromium precipitates in said sheet and to thereby produce a multiplicity of light transmitting microperforations through said sheet, the microperforations being primarily due to electrochemical action.

2. The process described in claim 1 characterized in that the stainless steel sheet has been fabricated from cast and rolled alloy.

3. An electrically controlled process for producing thin microperforated stainless steel sheet which comprises connecting a sheet of stainless steel having a thickness in the order of .0005" to .005" and containing intergranular iron chromium precipitates as the anode in an electrolytic cell having a non-polarizing electrolyte and a cathode and discharging direct current through said cell so as to produce a multiplicity of light transmitting microperforations through said sheet at the grain boundaries by dissolution of iron chromium precipitates without substantial reduction in thickness of the sheet.

4. An electrically controlled process for producing a perforated body which comprises connecting a sheet of iron chromium alloy having a thickness in the order of .0005" to .005", containing intergranular iron chromium

precipitates, and containing as essential elements a preponderance of iron and a lesser but significant amount of chromium as the anode in an electrolytic cell containing a non-polarizing electrolyte and a cathode and discharging substantially continuous unidirectional direct current through said cell for a time sufficient to produce a multiplicity of light transmitting microperforations substantially uniformly distributed through said sheet, said perforations being primarily due to electrochemical action.

5. The process described in claim 4 characterized in that the cathode comprises titanium.

6. The process described in claim 4 characterized in that after stainless steel sheet has been microperforated, it is impregnated with a microporous membrane producing material.

7. An electrically controlled process for producing microperforated stainless steel which comprises connecting a sheet of stainless steel having a thickness between approximately .0005" and .005", containing intergranular iron chromium precipitates and containing as essential elements a preponderance of iron and a lesser but significant amount of chromium as the anode in an electrolytic cell containing an electrolyte comprising a non-polarizing halogen containing solution and discharging direct current through said cell for a time sufficient to produce a multiplicity of light transmitting microperforations through said sheet, said perforations being primarily due to electrochemical action.

8. The process described in claim 7 characterized in that the halogen containing electrolyte is selected from the group comprising hydrochloric acid; hydrobromic acid; solutions of halogen salts which when dissolved hydrolyze to an acidic electrolyte, solutions of alkali and alkaline earth metal halogen salts, ammonium halogen salts and natural brine solutions.

9. The process described in claim 8 characterized in that the concentration of the hydrochloric acid does not exceed 7%.

10. An electrically controlled process for producing microperforated stainless steel sheet suitable for fabrication into liquid and air filters, diaphragms, separators and the like which comprises connecting stainless steel sheet consisting of a preponderance of iron and containing a minimum of approximately 11½% chromium having a thickness between approximately .0005" and approximately .005" as the anode in an electrolytic cell having a non-polarizing electrolyte and a cathode and discharging direct current through said cell for a time sufficient to produce a substantially uniform pattern of a multiplicity of light transmitting microperforations through said sheet, said perforations being primarily due to electrochemical action.

11. An electrically controlled process for the continuous rapid production of sheet filter material which comprises the provision of an electrolytic cell having a cathode and non-polarizing electrolyte in which a portion of a strip of stainless steel is immersed, said steel consisting of a preponderance of iron and containing a minimum of approximately 11½% chromium and having a thickness not substantially exceeding .005" and constituting the anode of said cell, discharging direct current through said cell while passing said sheet therethrough at a current density and for a time sufficient to produce a multiplicity of light transmitting microperforations through said sheet, said perforations being primarily due to electrochemical action.

12. An electrically controlled process for the continuous rapid production of a microperforated stainless steel sheet which comprises the provision of an electrolytic cell having a non-polarizing electrolyte and a cathode inert to said electrolyte, an elongated strip of stainless steel consisting of a preponderance of iron and containing a minimum of approximately 11½% chromium, a portion of said strip being immersed in the electrolyte and at

anodic potential in respect thereto, said strip having a thickness in the order of .0005" to .005", discharging direct current through said cell, the strip being connected as the anode, while passing said strip through the electrolyte at a current density, applied voltage and for a period of time sufficient to produce a multiplicity of light transmitting microperforations substantially uniformly distributed through said sheet, said perforations being primarily due to electrochemical action, thereafter cleaning said perforated sheet to eliminate retained electrolyte.

13. A microperforated stainless steel product produced by the process of claim 1.

#### References Cited

##### UNITED STATES PATENTS

2,462,045 2/1949 Wulff \_\_\_\_\_ 148—12  
2,755,238 7/1956 Turner \_\_\_\_\_ 204—33

2,947,674 8/1960 Andrisek et al. \_\_\_\_\_ 204—141  
3,238,056 3/1966 Pall et al. \_\_\_\_\_ 117—98

##### FOREIGN PATENTS

5 637,730 3/1964 Belgium.  
490,795 8/1938 Great Britain.

##### OTHER REFERENCES

Belyakov et al.: Zavodskaya Laboratoriya, No. 10, 1961, pp. 1192—1194.

10 Miller et al.: Metal Progress, November 1949, pp. 692—695.

Moneypenny: Stainless Iron and Steel, Chapman and Hall Ltd., London, 1954, vol. 2, pp. 190, 191, 201, 204 and 205.

15

ROBERT K. MIHALEK, *Primary Examiner.*

JOHN H. MACK, *Examiner.*