Jan. 23, 1951 H. V. TRASK **2,538,990**

ELECTROLYTIC PROCESS FOR PRODUCING IRON PRODUCTS

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Fig. 1

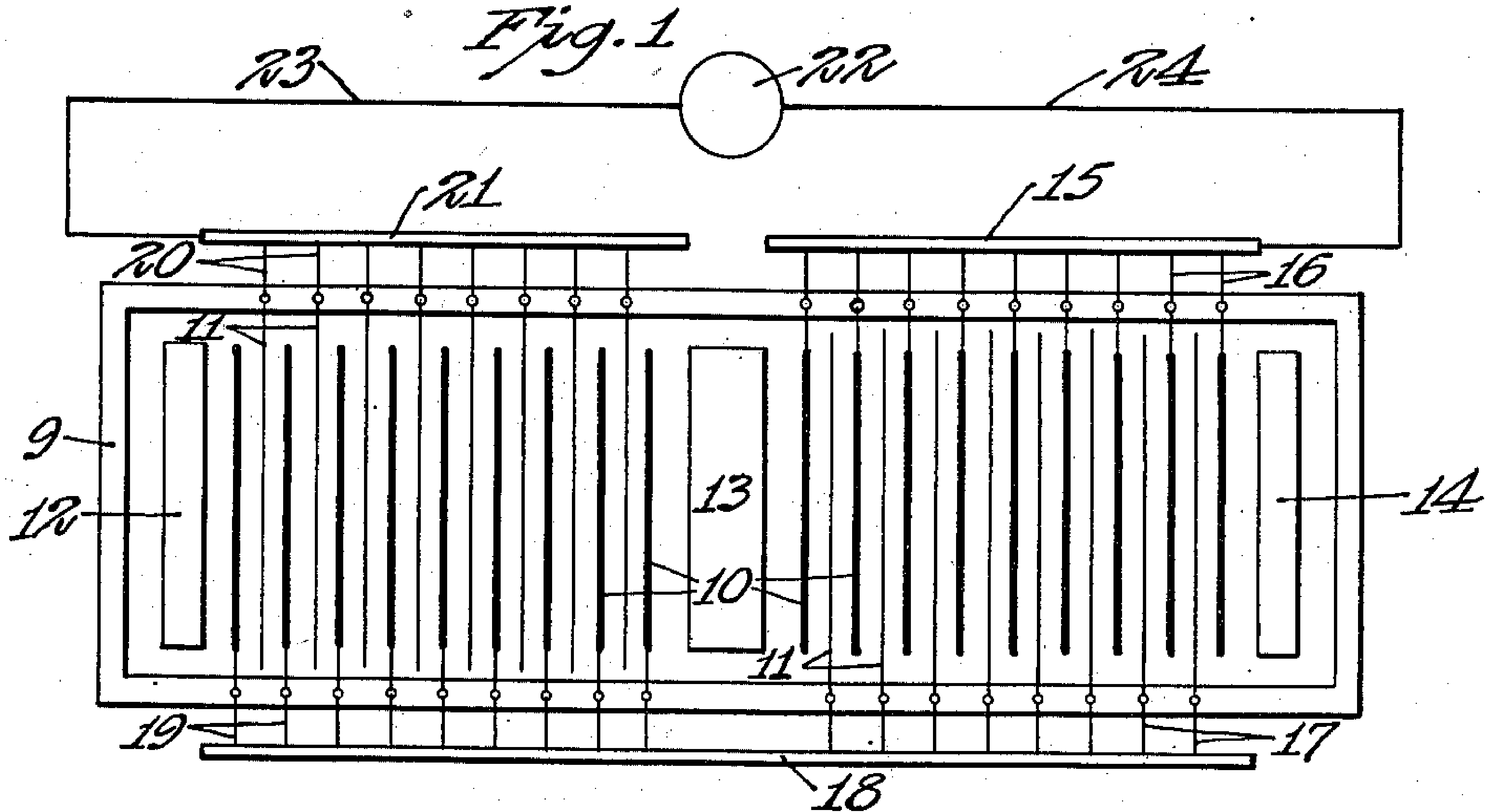


Fig. 2

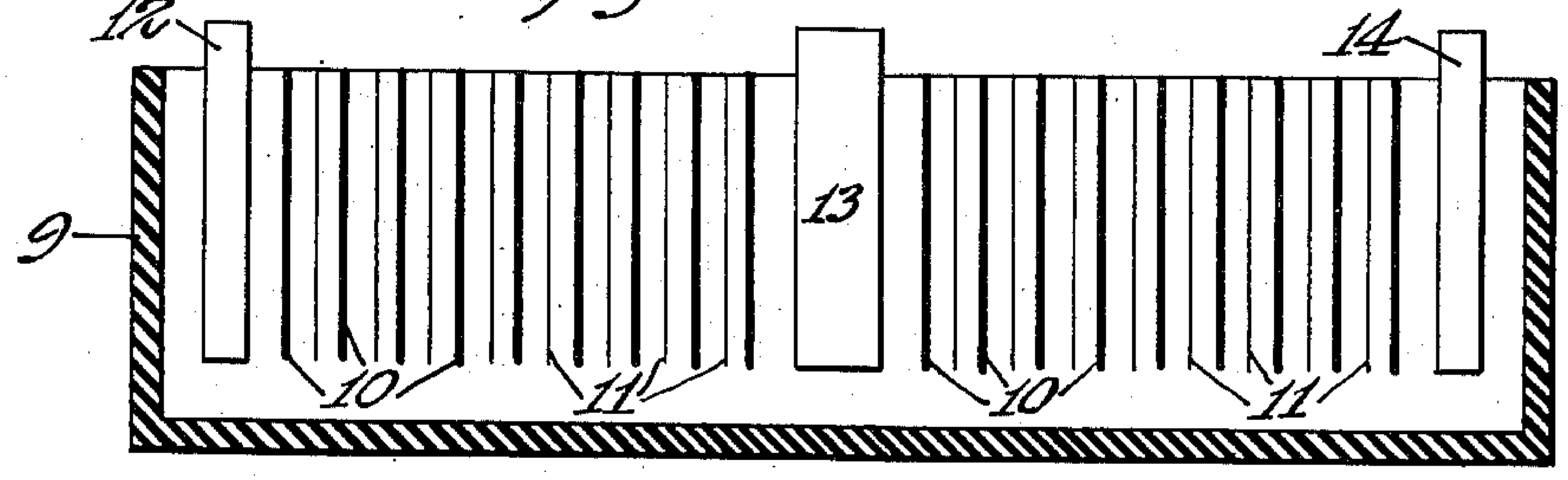
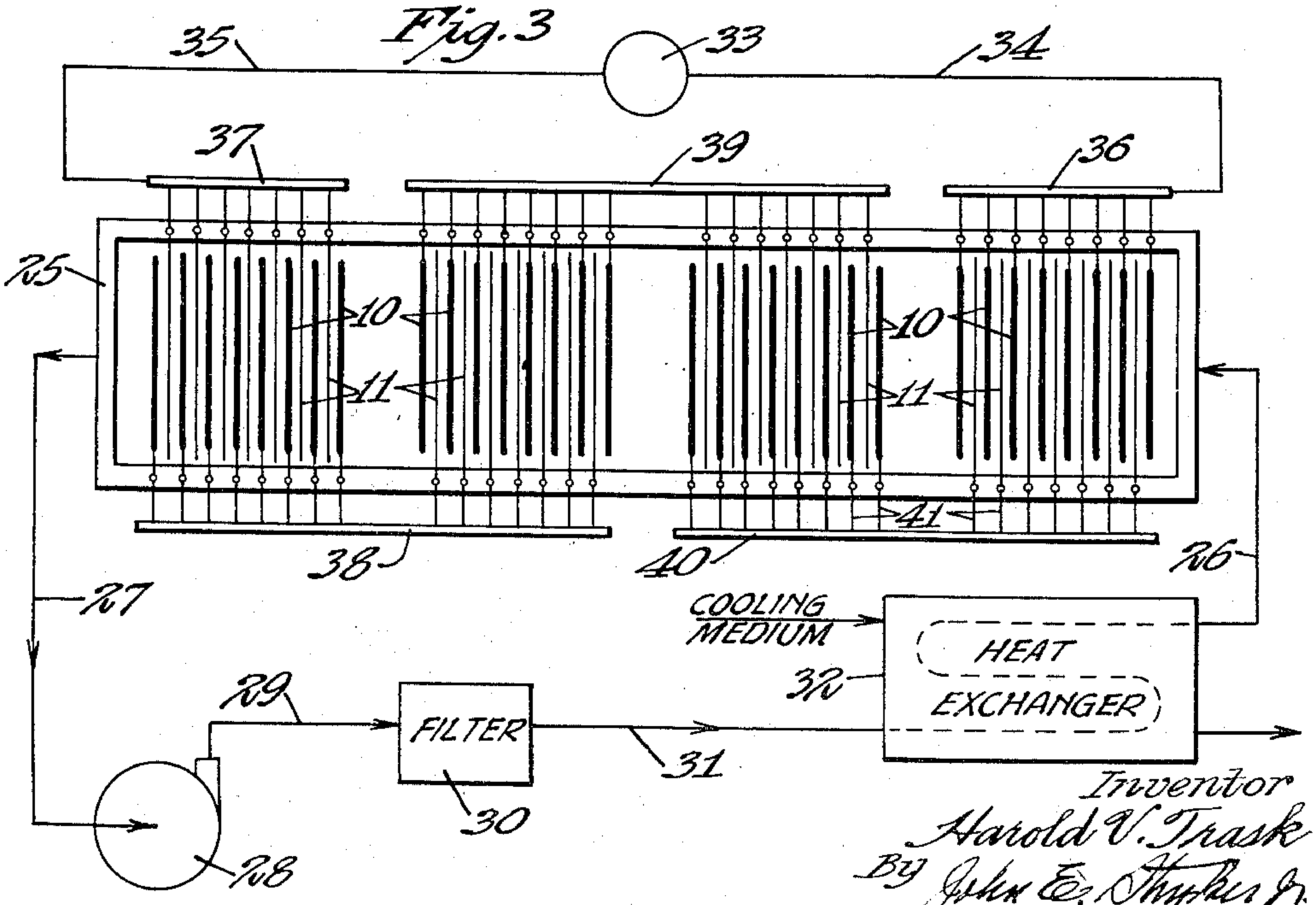


Fig. 3



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ELECTROLYTIC PROCESS FOR PRODUCING IRON PRODUCTS

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Fig. 4

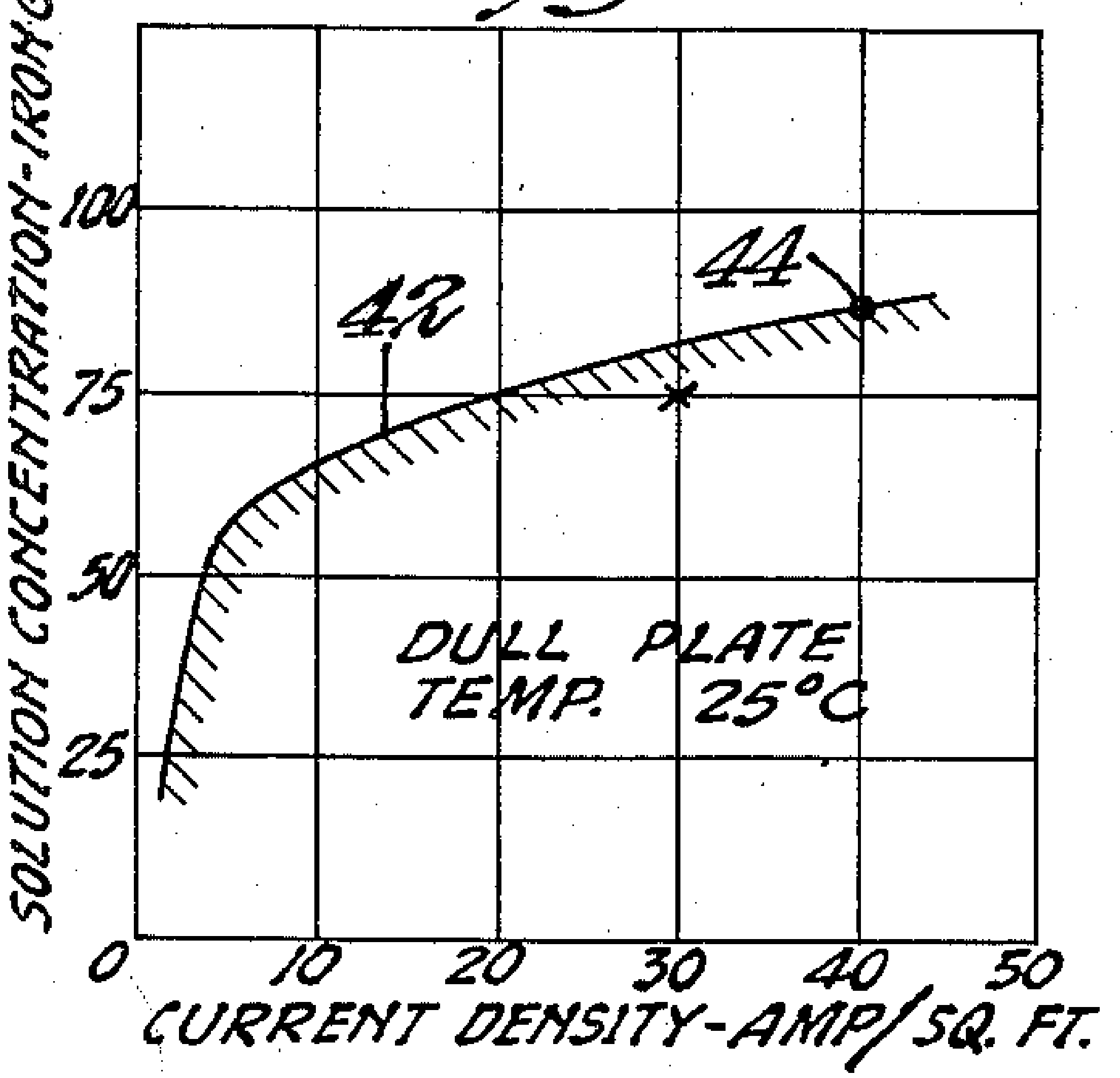


Fig. 5

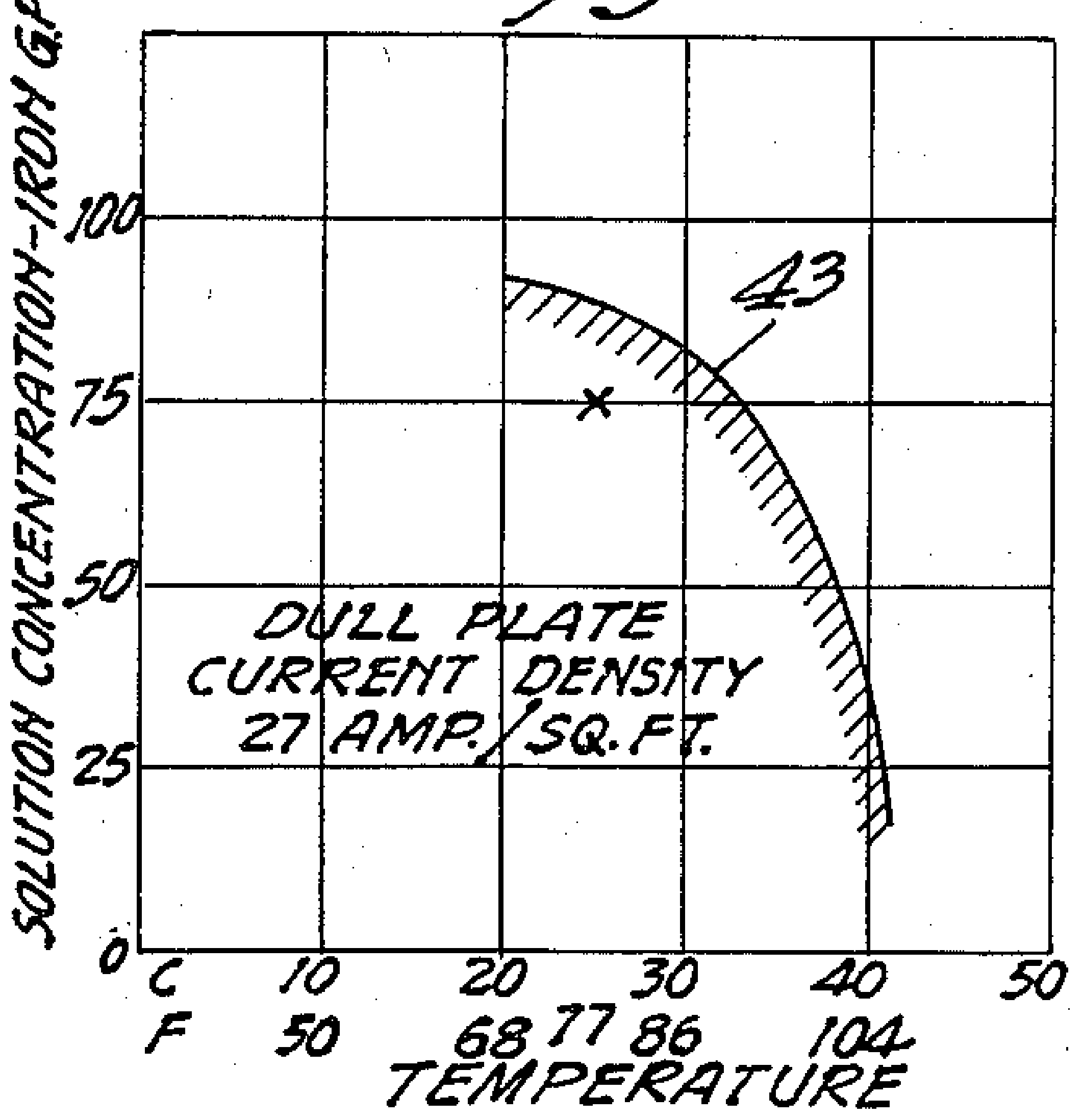


Fig. 6

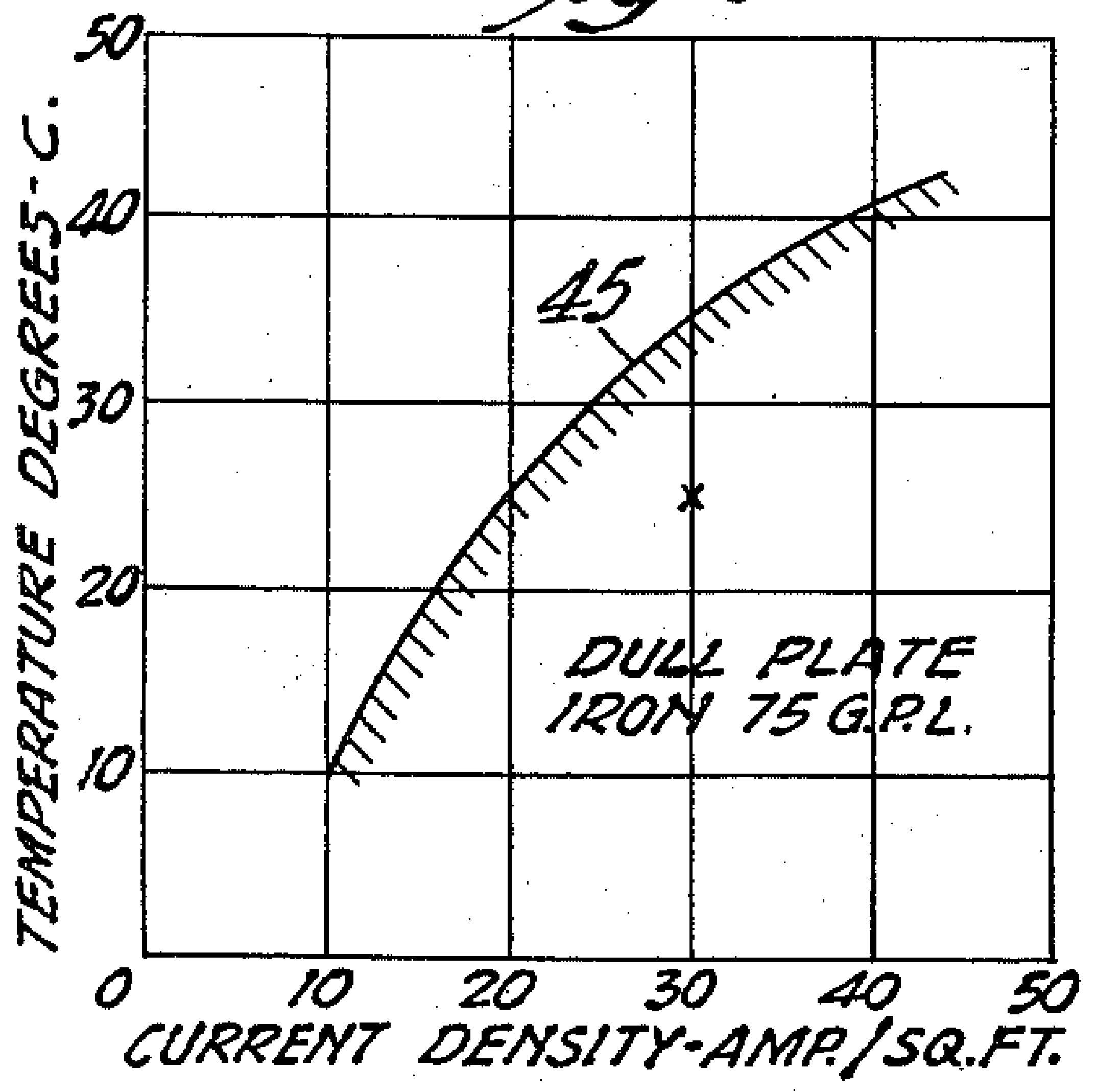


Fig. 7

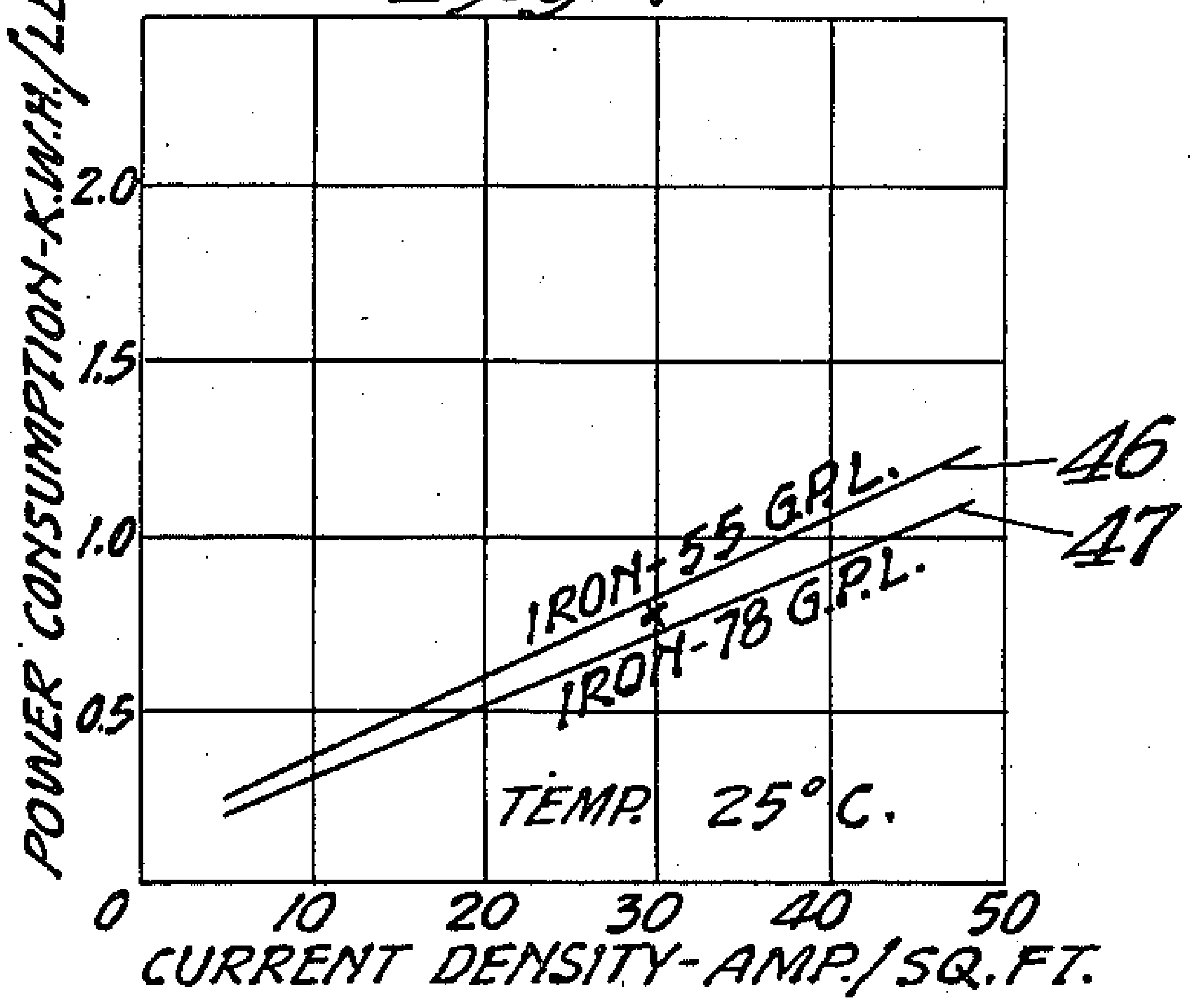


Fig. 8

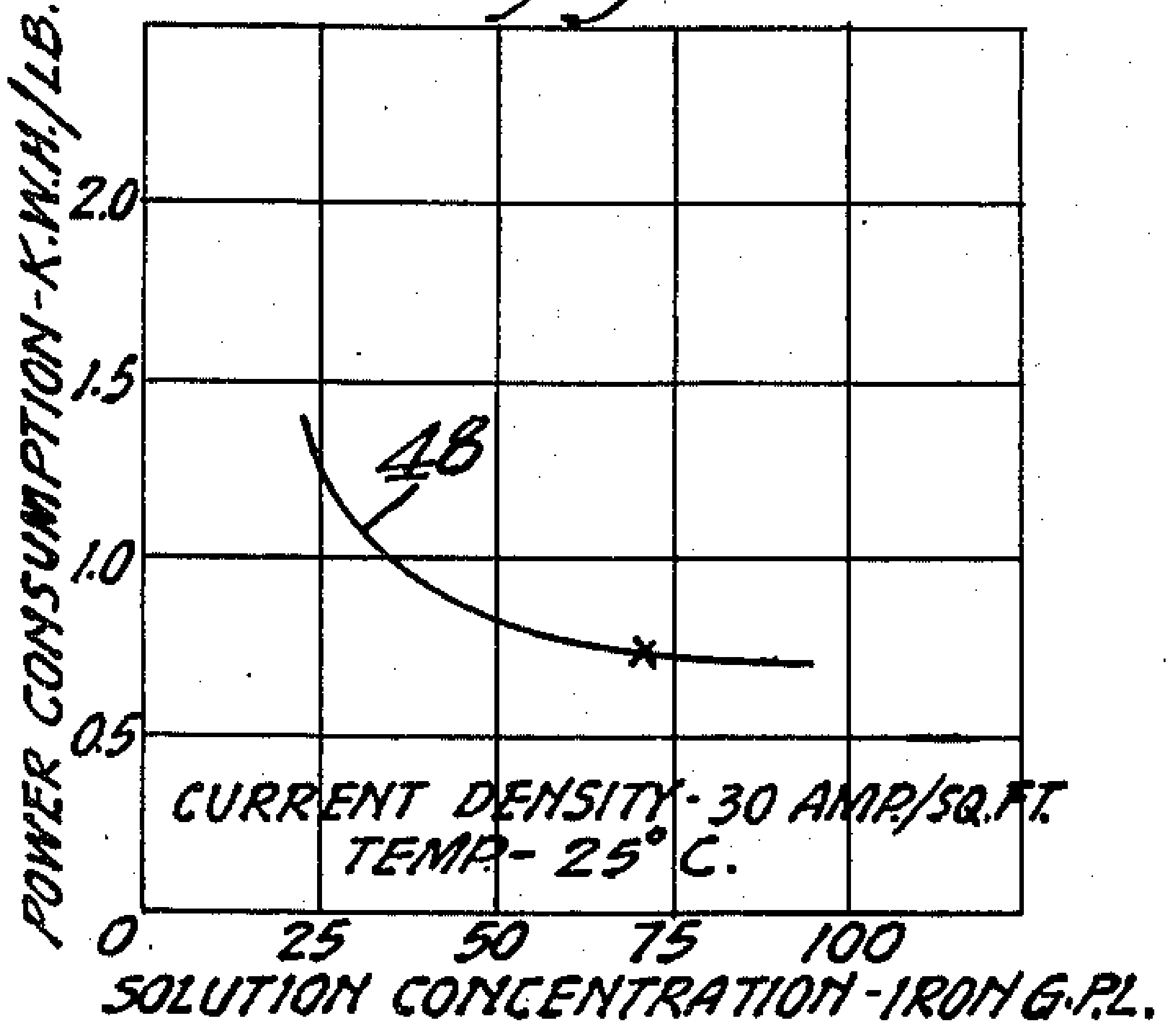
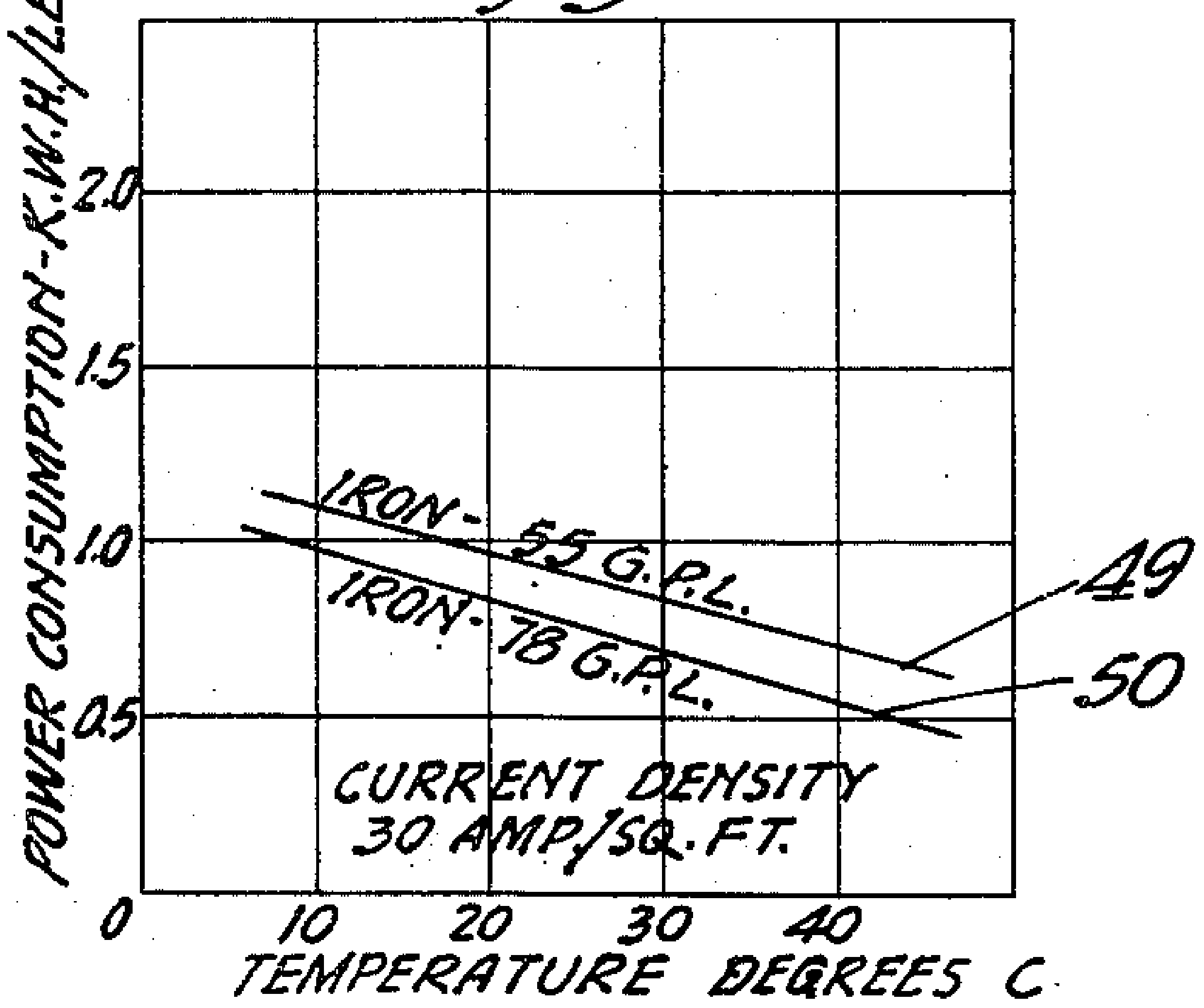


Fig. 9



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UNITED STATES PATENT OFFICE

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ELECTROLYTIC PROCESS FOR PRODUCING IRON PRODUCTS

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Application August 22, 1945, Serial No. 611,947

3 Claims. (Cl. 204—10)

This invention relates to the production by electrolysis of readily grindable iron of such composition that it is particularly adapted for use, after crushing and annealing, in cold die pressing operations where pure iron in the form of particles having equiaxial structure is required.

It is an object of my invention to provide an iron powder which is superior to known products of this kind in structure and composition for use in iron powder metallurgy.

Another object is to produce a low cost iron deposit which is characteried by the presence of a sufficient quantity of the oxide and hydroxide of iron to render the product readily grindable to particles of sizes suitable for use in iron powder metallurgy and from which the hardening constituents may be readily removed by simple annealing treatment.

A further and particular object is to provide a novel and economical process for producing brittle iron plate of the character described by electrolysis from relatively impure iron and whereby economies are effected by reason of the low capital investment required in plant and equipment, ease of control in the commercial production of a uniform product and low power consumption per pound of iron produced.

A still further object is to provide an electrolytically deposited, porous, brittle, dull iron plate which adheres well to the cathodes during deposition and is easily removable therefrom when the deposit has accumulated to suitable thicknesses.

Other objects will appear and be more fully pointed out in the following specification and claims.

My improved iron is sufficiently brittle as deposited at the cathode electrodes to permit economical crushing and contains iron oxides and iron hydroxides together with a small amount of chlorine totaling approximately 3% to 5% of the deposit. This product has a dark gray color and is herein called "dull iron plate." Other physical characteristics of my dull iron plate are its hardness, diamond scale, ranging from about 400 to 520, and its porosity which gives it a specific gravity ranging from approximately 6.3 to 7.25. By crushing or grinding it may be reduced to particles of the desired size (usually minus 100 mesh) and of equiaxial structure well adapted for use in iron powder metallurgy. The dull iron plate may be ground in a ball mill with air separation, or in any other

suitable grinder or pulverizer at low cost. It may be pulverized to minus 100 mesh sizes in a ball mill at the rate of 20 to 25 pounds per 100 pounds of balls per hour, whereas, ordinary electro-deposited iron pulverizes at a rate of from 0.25 to 1.0 pounds per 100 pounds of balls per hour. The hardening impurities, oxides and hydroxides may be reduced and the resulting gaseous elements together with any chlorine carried over from the electrolyte may be driven off by simple annealing treatment leaving a product which is more than 99.5% pure iron. The annealing treatment preferably comprises heating the ground product in a hydrogen atmosphere at approximately 800 degrees C. for from one to three hours, depending on the fineness of the product.

According to my process for making dull iron plate having the characteristics hereinbefore described, it is essential that the conditions present in the deposition cells with respect to (1) solution composition, (2) current density of the deposition and (3) temperature of deposition, shall be controlled and maintained within the limits presently to be described. The range of permissible values from a technical standpoint must be further limited to minimize the cost of production and facilitate control in commercial operations.

Solution composition

An electrolyte comprising a ferrous chloride solution has been found best suited for my purposes. An aqueous solution containing from 20 grams to 125 grams of iron per liter may be used. The limits of the solution concentration are interrelated with those of the temperature and current density of deposition. For example, the upper limit of iron concentration, as ferrous chloride, in the solution is somewhat dependent on the lowest temperature which can be economically maintained in the cell. If, as in most installations, it is not economical to keep the deposition temperature below 15 degrees C. the maximum concentration of iron is approximately 125 grams per liter for dull iron plate deposition. It is, however, much more economical to keep the iron concentration below this figure and I have found for most economical operation that the iron in solution should be maintained at approximately 75 grams per liter. With more dilute solutions it is necessary to increase the voltage to impress a given current density of deposition and this progressively increases the power consumed per pound of iron deposited. It is feasible, however, to obtain dull iron plate with maximum solution concentration ranging from about 67 to 87 grams of iron per liter where the current densities range from about 10 to 40 amperes per square foot and temperatures at or below 25 degrees C. are maintained in the cells.

A further necessary control involves hydrogen ion concentration of the solution. Its pH should be maintained between 3.0 and 5.5. A pH lower than 3 indicates the presence of excessive acid or ferric chloride and results in a bright iron cathode deposit which is unsuited for my purposes and is otherwise not satisfactory because of its poor adherence to the cathode plates. In practice the pH of my solution naturally adjusts itself between 5 and 5.5. With pHs above 5.5 the solution tends to hydrolize and a deficiency of iron in solution develops under conditions indicated by substantially higher pH values. The presence of ferric chloride in the solution is neither desirable nor necessary for the functioning of my process. Other additions to the electrolyte, such as ammonium chloride which has been used heretofore, are also detrimental.

Current density

In order to produce my dull iron plate economically, the current density between electrodes of the deposition cells must be maintained between certain values which are interdependent upon the concentration of iron in solution and temperature of deposition. In general, the higher the solution concentration the greater must be the current density at any given temperature within the feasible range. As hereinbefore indicated, practical limits of the current density are from about 10 to 40 amperes per square foot where the solution concentration ranges from a maximum of about 67 to 87 grams of iron per liter of solution and where a temperature at or below 25 degrees C. is maintained in the cell. With lower solution concentrations current at a density as low as 5 amperes per square foot may be caused to pass between the electrodes in the cells. The power consumed per pound of iron deposited increases in direct proportion to the current density and in inverse proportion to the temperature of deposition.

Temperature of deposition

In order to produce dull iron plate most economically the temperature of deposition should be maintained between 15 degrees and 35 degrees C. and preferably at approximately 25 degrees C. where the economical ranges of current densities and solution concentrations hereinbefore described are maintained. An unsatisfactory, bright, malleable deposit results when a temperature substantially above 40 degrees C. is reached in a cell of the character described.

Cells and electrodes

My process may be carried out in inexpensive open cells without diaphragms between the anodes and cathodes. As the source if iron, ingot iron plates of suitable thickness, preferably about one inch thick, may be used as anodes in the cells. These plates may contain up to .2% of carbon and substantial amounts of other impurities. For example, they may contain .03% carbon together with manganese, silicon and sulphur totaling approximately .10% and copper approximately .15%. As the cathodes from which the dull iron plate may be removed periodically and with ease, I employ flexible cathode starting sheets comprising stainless steel such as that containing approximately 18% chromium and 8% nickel. Sheets of $\frac{1}{16}$ to $\frac{1}{8}$ inch thickness have been found to be adequately stiff to remain straight in the cells while affording the flexibility necessary to permit ready removal of the brittle iron deposit by flexing.

The electrolyte for use in my process may be obtained by dissolving scrap iron, preferably of low carbon content, in hydrochloric acid. This concentrated solution of ferrous chloride is diluted so that it contains iron within the limits hereinbefore described and preferably about 75 grams of iron, as ferrous chloride, per liter of solution. The pH of this solution is maintained between 3 to 5.5 as indicated.

To control the temperature of deposition, inexpensive heat exchangers may be placed in the cells or built into the walls of the same, or the electrolyte may be circulated through a heat exchanger located exteriorly of the cells.

To illustrate my invention and not by way of limitation, reference is had to the accompanying drawings in which:

Figure 1 is a diagrammatic plan view of a suitable deposition cell;

Fig. 2 is a diagrammatic vertical section through the same;

Fig. 3 illustrates diagrammatically another arrangement of electrodes in a cell, together with means for filtering and cooling the electrolyte in a circuit exterior of the cell;

Fig. 4 is a graph showing the maximum solution concentrations which produce dull iron plate with various current densities and with a cell temperature of 25 degrees C;

Fig. 5 is a graph showing the maximum solution concentrations for dull iron plate with various cell temperatures and a current density of 27 amperes per square foot;

Fig. 6 is a graph showing the minimum current densities which produce dull iron plate at various temperatures where a solution concentration is maintained at approximately 75 grams of iron per liter of solution;

Fig. 7 shows graphs indicating the relation of power consumption to current density with certain solution concentrations and where the temperature of deposition is maintained at 25 degrees C. in producing my dull iron plate;

Fig. 8 shows a graph illustrating the effect of changes in solution concentration on power consumption in cells where the current density is maintained at 30 amperes per square foot and the temperature of deposition at 25 degrees C. in depositing dull iron plate, and

Fig. 9 shows graphs illustrating the relation between temperature of deposition and power consumption with certain solution concentrations and current density maintained at 30 amperes per square foot in dull iron plate deposition.

Referring to Figs. 1 and 2, the numeral 9 indicates a simple deposition cell containing iron anode plates 10, stainless steel cathode starting sheets 11 and heat exchangers 12, 13 and 14. The electric circuit includes a bus bar 15 having connectors 16 severally extending to the anodes 10 of a group, the cathode sheets 11 of which have conectors 17 extending to a bus bar 18. A second group anode plates 10 have connectors 19 extending to the bar 18 and the cathode starting plates 11 of this group have connectors 20 extending to a bus bar 21. A source of direct current

22 has conductors 23 and 24 connected to the bus bars 21 and 15 respectively. Anode plates of approximately one inch thickness are suitable for my purpose and these are preferably spaced two inches, center to center, relative to the adjacent stainless steel cathode sheets. With my preferred electrolyte solution in the cell 9 and by causing current to flow between electrodes at the density hereinbefore described, I obtain dull iron plate on the cathode sheets 11 with a voltage drop between adjoining electrodes 10 and 11 within the range 1.5 to 2 volts. The heat exchangers 12, 13 and 14 are supplied with brine or other cooling medium so that the temperature of the electrolyte is maintained within the limits described.

In the alternate arrangement shown in Fig. 3, the iron anode plates 10 and stainless steel cathode sheets 11 are arranged in groups as indicated in an open cell 25 and the electrolyte is fed into one end of the cell through a pipe 26 and continuously withdrawn from the other end through a pipe 27 by means of a pump 28. From the outlet of this pump the solution is fed through a pipe 29 supplying a filter 30 which removes solid particles of impurities and discharges and clear solution through a pipe 31 extending to a heat exchanger 32. From the latter the cooled electrolyte passes through the pipe 26 back into the cell 25. A cooling medium is supplied to the heat exchanger 32.

Direct current is supplied from a source 33 having conductors 34 and 35 extending to bus bars 36 and 37 respectively. Four groups of electrodes are shown in series between the bus bars 36 and 37. The electric circuit includes additional bus bars 38, 39 and 40 and individual connectors 41 extending therefrom to the several individual electrodes. Spacing of the electrodes is as hereinbefore described with reference to Figs. 1 and 2. Other arrangements of the electrodes in the circuit will be obvious to those skilled in the art and it will be evident that in commercial operations a large number of cells are connected either in parallel or in series in the circuit and that any suitable source of direct current may be provided. For example, the source may comprise a motor generator set or where a source of alternating current is available a rectifier of any suitable type may be used.

In operation from time to time as iron is deposited on the stainless steel cathode sheets 11, these sheets are removed from the cell and flexed to dislodge the brittle dull iron deposit after which they may be replaced in the cell to receive a further deposit of iron. Separation of the iron plate from the cathode sheets is facilitated if the coating is allowed to accumulate to a thickness of from ⅛ to ¼ inch. The flexing of the iron coated sheets may be performed manually by bending the sheets over a roller or bar, or otherwise in a machine designed for the purpose. After repeated use it is sometimes necessary to clean the cathode sheets before returning them to the tank and this may be accomplished by dipping them in dilute hydrochloric acid for a period of from 1 to 5 minutes. Cathode sheets of the character described are so durable that they may be used according to my invention almost indefinitely. The anode plates are merely replaced by new ones periodically as they are dissolved in the electrolyte. Other details of the operation are well known in this art and require no further explanation.

Figs. 4 to 9 inclusive show graphically the results of a large number of tests which I have conducted to determine the conditions necessary to produce dull iron plate at low cost. All tests were made with the electrodes spaced a distance equal to approximately two inches center to center in the cells. In Figs. 4 and 5 the curves 42 and 43 represent the highest solution concentrations which produce dull iron plate under the conditions indicated. The point 44 on the curve 42, for example, represents the maximum solution concentration, 87 grams of iron per liter, from which dull iron plate may be deposited with a current density of 40 amperes per square foot and temperature of 25 degrees C. I have determined that conditions represented by points below curve 42 will produce dull iron plate but that those represented by points above the curve will not at the temperature indicated, namely, 25 degrees C. My preferred solution concentration (75 grams of iron per liter of solution) and current density (30 amperes per square foot) is represented by a point X below the curve 42. As further indicated in Fig. 5, solution concentrations represented by points below the curve 43 produce dull iron plate with temperatures below 40 degrees C. and with current density at 27 amperes per square foot. With this current density and a temperature of deposition above 40 degrees C. dull iron plate cannot be obtained. Nor can such plate be obtained when the solution concentration exceeds about 90 grams of iron per liter and the deposition temperature is above 20 degrees C.

Graph 45 (Fig. 6) shows the relation between the minimum current densities which produce dull iron and the required temperatures where the electrolyte contains 75 grams of iron per liter of solution. This curve indicates the minimum current densities required from a technical standpoint and, as hereinbefore indicated, the upper limits are established by economic considerations.

Points on graphs 46 and 47, shown in Fig. 7, were obtained by computations from power consumption readings in kilowatt hours per pound of iron deposited based on a number of tests using different current densities and with the iron concentrations respectively equal to 55 grams per liter for graph 46, and of 78 grams per liter for graph 47 and with the temperature of deposition at 25 degrees C. The several tests on which these graphs were based resulted in dull iron deposits. As shown by these graphs the power consumed per pound of product is directly proportional to the current density of deposition.

Graph 48 (Fig. 8) was obtained from tests producing dull iron plate by plotting the power consumption per pound of iron deposit against solution concentration in grams of iron per liter of solution. In these tests constant current density at 30 amperes per square foot and deposition temperature at 25 degrees C. were maintained. It will be evident that progressively more power is consumed as the solution concentration is decreased below 87 grams of iron per liter and that as the solution concentration is reduced below about 50 grams of iron per liter the rate of power consumption increases rapidly. Under my optimum conditions and with a solution concentration of about 75 grams of iron per liter, approximately .75 kilowatt hour is required per pound of dull iron deposited. With a solution concentration equal to 25 grams of iron per liter of solution and other conditions unchanged, approximately 1.25 kilowatt hours is required per pound of dull iron plate.

Graphs 49 and 50 (Fig. 9) were also obtained from a number of dull iron plate deposition tests and by plotting the power consumption in kilowatt hours per pound against various temperatures of deposition with constant current density at 30 amperes per square foot. Solution concentrations equal to 55 grams of iron per liter were used for graph 49 and of 78 grams of iron per liter for graph 50. Upon comparing these graphs it will be evident that more power is required to obtain a dull iron deposit with the lower solution concentrations. Moreover, the power consumed is inversely proportional to the temperature of deposition.

By maintaining the preferred conditions hereinbefore described in the cells, I obtain a porous, brittle, coherent, dull iron deposit with current efficiencies above 100%. The reasons for this amazingly high efficiency are not entirely clear but it is thought that it is at least in part due to the porosity and coherent nature of my cathode deposit. The outer layer of iron as it is formed may act as an intermediate electrode between the anode plate and cathode sheet and electrolysis may cause decomposition of water in the pores between this outer layer and the cathode sheet whereby hydrogen and oxygen are liberated in these pores. Since the outer layer is iron in a very pure form it may combine with the liberated gases to form iron oxide and hydroxide under the conditions existing in the cell. Accordingly, current efficiencies above 100% may indicate that the iron is first deposited and later partially altered to the oxide and hydroxide state without affecting the carrying power of the current passing between the anode and cathode. Further substantiation of this theory may be found in the fact that analyses of the dull iron plate show that iron constitutes only from 95% to 97.5% of the product and that the hardening contaminants are oxide and hydroxide compounds which can be easily removed by annealing in a hydrogen atmosphere.

Dull iron plate when deposited under the conditions hereinbefore described adheres to the stainless steel starting sheets well and good cohesion is obtained as the plate increases in thickness. It also separates readily from the cathode sheets when the latter are flexed as described. These characteristics of the plate contribute in an important degree to economical production. Under conditions which cause the iron to be precipitated in the form of a non-adherent powder at the cathodes it becomes contaminated by the solid impurities which settle to the bottom of the cell from the anode plates and it is consequently difficult to remove from the cell and difficult to separate from the impurities. Such contaminated powder is also subject to excessive oxidation in the cleaning process.

The use of flexible, stainless steel cathodes containing substantial amounts of chromium and nickel has unique advantages in connection with my process wherein such cathodes exhibit a critical degree of adherence with the dull iron deposit which results in even surface accumulation on the cathodes and subsequent efficiency and economy in the removal of the deposit by simple flexing. It has been found that where it is attempted to operate with a pH of solution below 3, the deposit does not adhere to the stainless steel cathode sheets and causes short circuits due to the peeling off of the deposit. Moreover, where

temperatures of deposition above the critical values herein described are maintained in a cell containing an electrolyte of low iron concentration, viz., less than 125 grams of iron per liter of solution, a bright iron accumulates on the stainless steel cathode which is bonded so securely thereto that it cannot be removed economically as by merely flexing and/or scraping treatment. It will thus be evident that peculiar and unexpected functional advantages are derived from the use of flexible, stainless steel cathode sheets according to the present invention.

My coherent dull iron plate may be ground at low cost to sizes suitable for iron powder metallurgy and when finely divided has excellent structure for this purpose in that the individual particles have substantially equiaxial structure rather than a flat structure which results from attempts to grind bright iron deposits. As further hereinbefore pointed out, the ground product may be purified, without destroying its advantageous equiaxial structure, by simple annealing treatment in a hydrogen atmosphere. Analyses of a number of specimens of my dull iron plate show the following ranges of composition in percentages by weight:

	Percent
Total iron as stripped	95–97.5
Chlorine as stripped	.3–.6
Weight loss after heating in nitrogen at 950 degrees C. for one hour	1.00–1.55
Weight loss after heating in hydrogen at 950 degrees C. for one hour	2.00–3.55
Total iron after reduction	99.5–99.9

After the crushing and annealing treatment measured quantities of the powder may be placed in dies and then pressed to the die shape without the application of heat. Pressures of the order of magnitude of 30 to 60 tons per square inch are used. The resulting self-sustaining bodies are then removed from the dies and subjected to a sintering temperature to unite the component iron particles. The bodies so formed from my product have great strength, homogeneous structure and other controlled properties. Test bars formed in this manner from my dull iron plate under 30 tons per square inch pressure and sintered for 1½ hours at 850 degrees C. have had tensile strength ranging from 23 thousand to 26 thousand pounds per square inch and show elongation under test equal to from 7 to 10 per cent in one inch. It will be evident that the pure iron powder may be mixed with other substances to modify the properties of the end product.

The present application is in part a continuation of my application, which has been abandoned, Serial No. 560,783, filed October 28, 1944, for patent for Dendritic Iron Product and Process for Making the Same.

Having described my invention, what I claim as new and desire to protect by Letters Patent is:

1. The process for making brittle, porous iron plate by electrodeposition which comprises, maintaining in a cell a solution composed substantially entirely of ferrous chloride and water at a concentration within the range 20 to 125 grams of iron per liter and at a pH from 3 to 5.5, subjecting said solution to electrolysis between a soluble iron anode and a cathode at a current density between 5 and 40 amperes per square foot and at a temperature within the range 15° to 40° C., the values within said ranges being selected to produce a brittle, dull gray deposit having specific gravity from 6.3 to 7.25.

2. The process for making brittle, porous iron plate by electrodeposition which comprises, maintaining in a cell a solution composed substantially entirely of ferrous chloride and water at a concentration within the range 67 to 87 grams of iron per liter and at a pH from 3 to 5.5, subjecting said solution to electrolysis between a soluble iron anode and a cathode at a current density between 10 and 40 amperes per square foot and at a temperature within the range 15° to 35° C., the values within said ranges being selected to produce a brittle, dull gray deposit having specific gravity from 6.3 to 7.25.

3. The process for making an iron powder which comprises, maintaining in a cell a solution composed substantially entirely of ferrous chloride and water at a concentration within the range 20 to 125 grams of iron per liter and at a pH from 3 to 5.5, subjecting said solution to electrolysis between a soluble iron anode and a cathode at a current density between 10 and 40 amperes per square foot and at a temperature within the range 15° to 40° C., the values within said ranges being selected to produce a brittle, dull gray plate having specific gravity from 6.3 to 7.25, pulverizing said plate to particles of sizes and shapes suitable for compaction in forming dies and annealing the resulting powder in a reducing atmosphere and at a low fritting temperature to produce a powder containing less than .5% of impurities.

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