Nov. 7, 1950 J. L. TURNER ET AL 2,529,237

ELECTRO-RECOVERY OF METALS

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Fig. 1

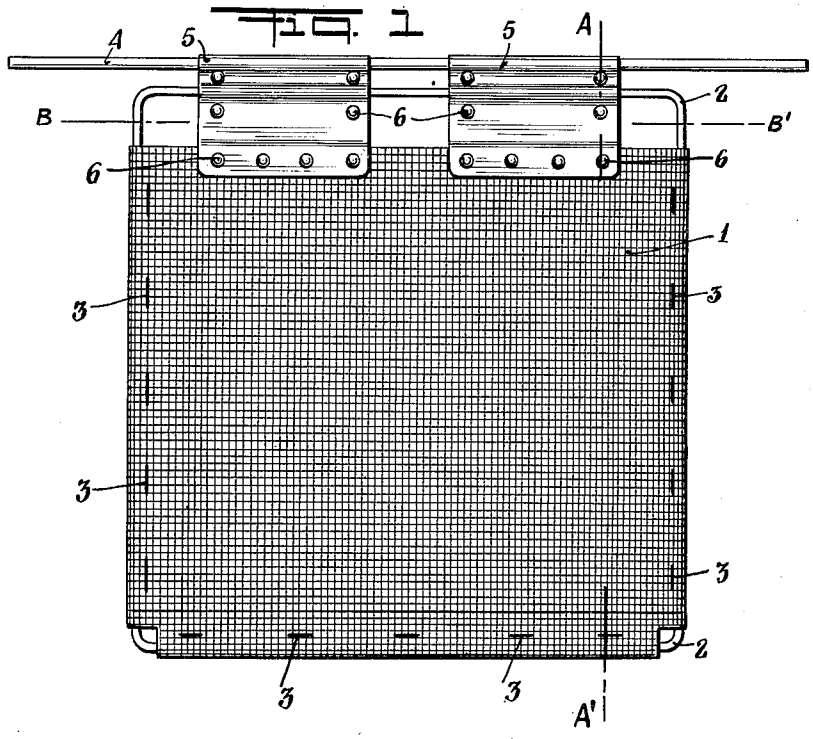


Fig. 2

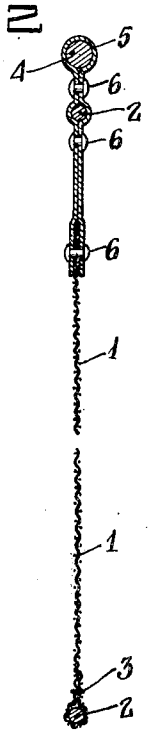
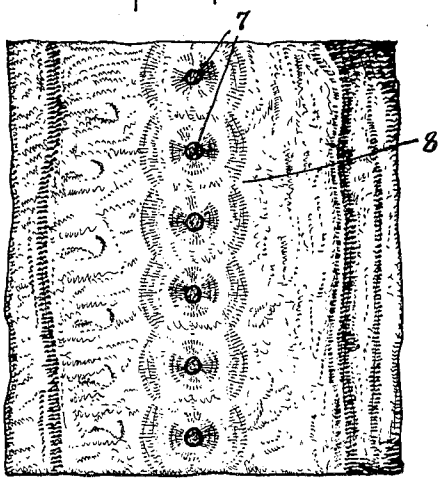


Fig. 3



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ELECTRO-RECOVERY OF METALS

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3 Claims. (Cl. 204—10)

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Our invention concerns the electro-recovery of metals by the electrolysis of solutions containing compounds of the metals. More particularly, it relates to an improved method of preparing metallic products, which includes the step of electrolytically depositing a relatively large amount of metal upon a special type of cathode. It also embraces the novel cathodes employed in this method, as well as the heavy, compact and substantially homogeneous electrodeposits that are formed. In its preferred embodiment it deals with the production of iron powder by a process that includes electrodeposition of iron upon such a cathode.

The electro-recovery of metals by the electrolysis of solutions of metal compounds, employing an electrolytic cell in which the metal is deposited upon a cathode, has long been known and is widely practiced. The term "electro-recovery" includes electro-winning, electro-refining and electro-forming. The object in every case is to recover the deposited metal or to produce an article composed essentially thereof, rather than merely to apply a very thin coating of the deposited metal to an article made of some other metal, as is done in electro-plating.

It is desirable in electro-recovery processes to deposit a large amount of metal upon the cathode within a short time. Usually, and especially in electro-refining, one wishes to recover the deposited metal in a very pure form. Consequently, it is the practice in such cases either to construct the cathode of the same metal as that to be recovered, the metal employed being likewise of high purity, or else to strip the deposit of pure metal from the cathode after the deposition has been completed. The cathodes used in electro-recovery processes generally consist of a metal sheet which is often specially treated to facilitate stripping off of the deposited metal.

The various electrolytes and types of electrolytic cells used in the electro-recovery of metals are known to those skilled in the art. The same is true of the operating conditions of the electrolysis, such as concentration of electrolyte, temperature, current density and the like. The metals most commonly recovered by electrolysis are gold, silver, copper, manganese, iron, nickel, cobalt, zinc, cadmium, tin and lead. Our improved method and special tytpe of cathode may be employed for the electro-recovery of any of these metals. They are particularly suited for the electro-recovery of base metals of the group consisting of copper, manganese, iron, nickel, cobalt, zinc, cadmium, tin and lead. The greatest advantages accrue from their use in the electro-recovery of iron. Next in importance is the application of our invention to the electro-recovery of manganese.

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The nature of the metal deposit formed upon the cathode is of great importance for the practicability of the electro-recovery processes. Great difficulty is encountered when seeking to obtain heavy deposits quickly. The deposits exhibit a marked tendency to develop cracks, followed by foliation and chipping off of metal particles into the electrolyte. Nodules and trees are formed resulting in uneven deposits which in turn may cause warping or buckling of the cathode. Any such protrusions, if substantial enough, will result in short-circuiting the cell or in damage to adjacent diaphragms or anode bags, and will interfere with the easy removal of the deposit from the cell. These undesirable tendencies may be reduced by lowering the current density, particularly during the early stages of the deposition, but the use of such low current densities so retards the rate of deposition as to render the process uneconomical in many cases.

It is also difficult to obtain the proper degree of adherence between the deposit and the cathode. Usually, only thin deposits can be readily stripped from the cathodes, but it is uneconomical to frequently interrupt the electrolysis for this purpose. Insufficient adherence will prevent the formation of the desired heavy deposits. Many attempts have been made to regulate the degree of adherence by pretreatment of the cathode surface. It has generally not been possible to obtain a deposit that was sufficiently adherent to avoid peeling throughout the cathode area during deposition and yet adequately weakened at the juncture between deposit and cathode to allow ready stripping and removal of the deposit. This has made it necessary in many cases to construct the cathode of the same metal and of the same purity as the deposit and thus to render unnecessary the subsequent removal of the deposit from the cathode.

It is the object of our invention to overcome or at least substantially reduce the aforesaid difficulties, and to provide a practical and economical method of preparing metallic products, which includes the step of electrolytically depositing a large amount of metal within a relatively short time. We have found that this object can be accomplished by the use of the herein described, special type of cathode in place of the sheet metal cathodes heretofore employed. By the use of this special type of cathode one can obtain

heavy, compact and substantially homogeneous electrodeposits possessing new and useful properties. The precise nature of the cathode and the many advantages resulting from its use in the electro-recovery of metals, will become apparent from the following detailed description.

The outstanding feature of the special type of cathode employed according to our invention, is that the greater part, if not all, of its effective area is composed of a thin, openwork pattern of electrically conductive material. It differs from the usual sheet metal cathode by reason of the numerous openings in the pattern, which permit the electrolyte to circulate freely, i. e., to pass through the cathode from one side to the other, during the critical, early stages of the electrodeposition. This produces a more uniform and better adhering deposit at the start than is obtainable with the prior art, sheet-metal cathodes. The metal to be recovered is first deposited within these openings and around the electrically conductive material. Thus a firm basis for the deposition of additional metal is obtained and the tendency of the deposit to peel, particularly during the early stages of the deposition, is greatly reduced. The openings also serve to provide maximum initial surface area with a minimum amount of material, while retaining sufficient mechanical strength. One may, and generally does, continue the deposition until the openings are completely filled, and a heavy, compact and substantially homogeneous slab of deposited metal, having the open work pattern embedded therein, is formed. The metal deposited within the openings serves to firmly unite the portions of the deposit that lie on opposite sides of the cathode, thus serving to effectively anchor the heavy, metal deposits to the cathode.

The thin, open-work pattern preferably consists of a woven wire fabric, such as screen or gauze. It may also be composed of a highly perforated sheet or of parallel strips or strands. The particular design of the pattern is largely a matter of choice and convenience. We have found that patterns may be employed in which the total of the projected areas of the openings amount to from about 15% to about 90%, preferably from about 40% to about 80%, of the projected area of the pattern. In the case of a woven wire screen, this corresponds to from about 2 to about 40 mesh, preferably from about 12 to about 24 mesh, employing wire of from 0.10 to about 0.001 inch, preferably 0.05 to 0.008 inch, in diameter. Since it is generally desired that the deposit completely fill the openings in the pattern, and one does not wish to make the cathode unnecessarily large, the width of the openings should not exceed 0.5 inch and, preferably, should be less than 0.10 inch. It will be found, when employing such open-work patterns, that the ratio of their actual current density to their apparent current density (calculated as a continuous sheet of equal dimensions) is from about 4:1 to about 1:2, preferably, from about 1:1 to about 1:2.

The open-work pattern must, of course, be composed of an electrically conductive material that can be fabricated in the desired form. In most cases one will employ a metal as the cathode material, and often the same metal as is to be deposited thereon. Thus we prefer to make the pattern of iron when recovering iron. However, when recovering manganese, we prefer to use copper, since copper can readily be fabricated into the desired form and will alloy with manganese to form a commercially desirable product.

It is also possible for special applications to make the open-work pattern of a plastic substance, such as rubber or a synthetic resin which has been impregnated or coated with a conductive material, such as graphite or a metal powder.

The open-work pattern must possess sufficient mechanical strength to carry the desired, heavy deposit of metal which, however, to a large extent becomes self-supporting as it accumulates. Owing to its many openings the pattern will be flexible and must, therefore, be supported within a rigid frame. This frame, which is also made of electrically conductive material, serves the further purpose of aiding in the distribution of the current throughout the entire effective area of the cathode. Generally, and particularly in the case of a woven fabric, the open-work pattern will possess a certain amount of resiliency and elasticity, which properties contribute to the desired result, as will be pointed out hereinafter. Ordinarily the cathode will be of a stationary type and will consist of the open-work pattern held tautly within a rectangular frame. However, the cathode may be cylindrical or disk-shaped, particularly if it is of the rotating type.

Our new cathodes are employed in the known electro-recovery processes and apparatus in place of the usual sheet-metal cathodes. The difficulties heretofore encountered when attempting to obtain large metal deposits within a short time are either greatly reduced or entirely eliminated due to the special characteristics of the open-work pattern. No special control of current densities or pretreatment of the cathode to insure the proper degree of adherence of the deposit are necessary. It is possible without difficulty and while applying relatively high current densities (as compared with prior practices) to obtain compact, substantially homogeneous deposits that are at least 0.03 inch thick. Many of the metals subject to electro-recovery may be deposited upon our new cathodes until the thickness of the layer produced exceeds 0.1 inch, and some of them, especially iron, will form deposits considerably over 0.3 inch thick. In most cases the electrodeposition will be continued until the deposited metal has entirely filled the openings in the pattern and has formed a thick slab having the pattern embedded therein. However, in some cases, particularly where the pattern possesses relatively large openings, it may be desirable without sacrificing the advantages to be derived from our inventon, to terminate the electrodeposition before the metal deposit has entirely filled the openings.

After completion of the electrolysis the cathodes are removed from the cells and the open-work pattern, together with the metal deposited thereon, is removed from the supporting frame, which may then be re-used. The breaking away of the open-work pattern and metal deposits thereon from the frame can be facilitated in various ways. For example, if the open-work pattern is folded over the frame, very little metal will be deposited on the frame and this can easily be chipped away. Also one can minimize deposition of metal on the frame by coating it with a nonconductive material, which can be done after the pattern has been attached thereto by welding or the like. In most cases the electrodeposits will have been built up to the form of fairly thick, continuous slabs in which the pattern is embedded about midway between the faces, the deposited metal completely filling the openings and transfixing the pattern. While the deposited metal is substantially homogeneous, its crystal

structure and the nature and amount of impurities therein will clearly indicate its electrolytic origin.

The heavy, electrodeposits obtained in accordance with our invention will generally be processed without prior removal of the embedded cathode material. Such processing may consist in pulverization, rolling, forging, melting, or the like. For this reason, it is often preferred to make the open-work pattern of the same metal as is to be deposited thereon. However, the metal need not be of the same purity as that of the deposit, because the weight of the pattern usually represents but a small fraction of the weight of the deposit, so that the amount of impurity introduced by way of the pattern is insignificant for the whole. In some cases, even though the pattern and the deposit are composed of different metals, they can simply be molten together to produce a valuable alloy. The open-work pattern, particularly when it is in a conventional form, such as a woven wire screen, and is composed of metal having no unusually high degree of purity, is generally quite inexpensive and can, therefore, economically be replaced within the supporting frame of the cathode, which may then be used for further depositions.

It is not possible to remove the deposited metal from the open-work pattern by the usual stripping procedure. In those cases in which it may be desired to separate the cathode material from the deposited metal, this must be accomplished by other means. Such cases will only occur where the material of which the pattern is composed differs substantially from the deposited metal. Separation can then be effected by taking advantage of the difference in properties between the two materials. For instance, the deposit with the cathode material embedded therein may be pulverized and the particles of the respective materials separated by a magnetic process. One may also utilize a wide difference in melting points. For example, one can melt an electrodeposit of lead off from an open-work pattern composed of stainless steel. In this case it is not necessary first to remove the pattern and deposit from the frame. Both the frame and the open-work pattern may be used again after the deposit has been molten off.

All of the reasons why our special type of cathode possesses the considerable advantages previously mentioned, as compared with the usual sheet-metal cathodes, are not fully understood. We, therefore, do not wish to limit ourselves to any particular theory of operation. However, we believe that the many openings in the open-work pattern bring about a better circulation of the electrolyte during the early stages of the deposition and that this results in the more uniformly and strongly adhering deposit adjacent to the cathode. There appears to be less danger that local depletion of the electrolyte will result in excessive formation of hydrogen. Furthermore, it is probable that the flexibility and resiliency of the pattern allows it to absorb and equalize the stresses that are set up during the early stages. Undoubtedly the open-work pattern provides a far better anchorage for the deposit and thus serves to minimize foliation.

Our invention is particularly applicable to the electro-winning of iron. We shall, therefore, describe it in detail with reference to the production of metallic iron products, specifically iron powder. Its application to the production of other metal products will then be obvious. In the electro-winning of iron one generally employs an iron chloride solution, preferably ferrous chloride, as the electrolyte. The apparatus consists of an electrolytic cell or rather a plurality of such cells of any suitable design. Preferably the cells are so constructed as to provide compartments separated by a diaphragm for the segregation of catholyte liquor from anolyte liquor. In this apparatus the iron is deposited on the cathodes and chlorine gas is evolved and liberated at the anodes. The latter are usually composed of an electrically conductive, inert material such as carbon.

The special type of cathode to be employed in the aforesaid apparatus according to our invention, is illustrated in the accompanying drawings. These drawings show one form of such a cathode and it is obvious that a great number of variations and modifications thereof are possible without departing from the scope of our invention.

In the drawings:

Fig. I is a vertical view of such a cathode assembly.

Fig. II is a cross section along the line A—A' of the cathode assembly shown in Fig. I.

Fig. III is a greatly enlarged cross section of a portion of the screen shown in Figs. I and II embedded within the final, heavy electrodeposit of iron.

In the cathode assembly shown in Figs. I and II the reference numeral 1 represents an ordinary iron wire screen that forms practically the entire effective area of the cathode. This screen is 16 mesh, i. e., has 256 openings per square inch, and is composed of iron wire of 0.01 inch in diameter. It is supported within a rigid frame 2 made of a heavy gauge, iron rod to which it is secured by folding it over the rod and holding the double thickness together by means of staples 3. The frame 2 is connected to a copper bus bar 4 by means of sheet-iron loops 5. These loops serve to conduct and distribute electricity to the screen and the frame and are firmly attached thereto by means of rivets 6. When in use, the cathode assembly is hung in the electrolytic cell, the ends of the copper bus bar 4 resting upon opposite sides of the cell. The level of the electrolyte is indicated in Fig. I by the line B—B'.

In Fig. III reference numeral 7 represents a cross section of the iron wire of which the screen 1 is composed. 8 represents the final, heavy, iron deposit. The crystal structure of the iron is indicated. It radiates from the wires of the screen. The deposit tends to vary slightly at different stages of the deposition and thus becomes striated in cross section. One can visualize from this striation how the deposit was first built up about the wires, filling up the openings and finally merging to form a continuous slab. The iron wire screen used in the cathode illustrated weighs about 0.11 pound per square foot. We have experienced no difficulty in forming iron deposits weighing more than 200 times as much as the embedded screen.

A suitable composition of the electrolyte for use in the electrolysis of an iron chloride solution is as follows:

F as $FeCl_2$	grams per liter	80 to	120
Fe as $FeCl_3$	do	1 to	2
NaCl	do	30 to	80
pH		0.5 to	2.0

At the start of the electrolysis this solution will form both the catholyte and the anolyte, but

during the early stage of the electrolysis and prior to the liberation of chlorine gas at the anode, ferric chloride will build up in the anolyte. Either brittle or ductile iron may be produced, depending primarily upon the temperature at which the electrolyte is maintained during the electrolysis. When the temperature is held below about 60° C. brittle iron is produced, while at higher temperatures ductile iron is obtained. Generally speaking, the lower the temperature the more brittle will be the iron and conversely the higher the temperature the more ductile it will be. The electrolysis can be satisfactorily conducted with our special type of cathode within a wide range of current densities on the cathode. If brittle iron is desired the current density may be from about 5 to about 50 amperes per square foot of apparent cathode area (calculated as a continuous sheet of equal dimensions). Preferably the apparent current density ranges from about 15 to about 30 amperes per square foot. Higher current densities may be employed when producing ductile iron and in that case the apparent current density may range from about 5 to about 225 amperes per square foot, preferably from about 50 to about 100 amperes per square foot.

As the electrolysis proceeds, iron is deposited upon the surfaces of the open-work pattern within the supporting frame of the cathode assembly. Gradually the deposit grows and completely fills the interstices of the pattern forming a substantially homogeneous mass of iron transfixing the pattern and, to a certain extent, still evidencing its design. As additional iron is deposited, the mass gradually assumes the shape of a thick slab whose surfaces no longer evidence the design of the pattern. In the electro-recovery of iron we prefer to continue the deposition at least up to this point in order to realize in full the benefits of our invention. After the desired amount of iron has been deposited on the cathode, the cathode assemblies are removed from the cells and washed. The electrolytically deposited mass of iron having the open-work pattern embedded therein is then detached from the supporting frame. This presents no difficulties. In the cathode assembly shown in the drawings the frame is to a large extent protected by the iron wire screen that is wrapped around it, and the deposit does not adhere strongly to the frame. It can easily be chipped or broken away and the little that adheres can be scraped off, thus preparing the frame for re-use. If desired, in order to facilitate removal of the deposit, the frame may be coated with an insulating composition, such as a varnish or lacquer. If the coating is applied after the open-work pattern has been attached to the frame, the deposit will be confined to that portion of the open-work pattern that lies within the frame, thus further simplifying the removal of the entire deposit and embedded pattern from the frame.

When the electrolysis has been controlled to yield brittle iron, the deposit with the iron screen embedded therein may be pulverized to any desired particle size. It is preferable to conduct this operation in several steps. Thus, a preliminary crushing, for instance in a jaw crusher, followed by a further pulverization such as is attained in a ball mill, is recommended. In this manner the deposited iron and embedded screen may be reduced to a fineness of 100 mesh or less. Generally, about 80 to 100% by weight of the iron screen is pulverized with the deposited iron. Any portions of the screen that are not reduced to the proper particle size may be readily separated by screening. It is desirable, in order to avoid oxidation of the iron to carry out the pulverization in a neutral atmosphere, e. g., in the presence of nitrogen or CO_2 gas. In most industrial applications of the present invention, the small amount of pulverized iron wire screen present in the metallic iron powder will not be objectionable. In fact, under the conditions just described, the screen will constitute only from about 0.33% to about 0.5% of the weight of the deposited iron. Of this amount under normal conditions at least four-fifths is pulverized and the remainder removed by screening. Assuming that the composition of the cathode wire screen is 98% Fe with 2% impurities and that the electrolytically deposited iron is 99.99% pure (analysis of annealed deposit) the purity of the final iron powder containing all of the pulverized iron screen, i. e., about 0.5% of the total, will be 99.98%, representing a lowering of purity of only 0.01%.

When the conditions of the electrolysis have been controlled to yield ductile iron, the mass of deposited iron in which the screen is embedded may be directly processed further, for instance, rolled or pressed out into sheets. In this case the presence of the embedded screen within the deposited iron will not be objectionable nor interfere in any way with the rolling or pressing. In fact, in certain instances, depending upon the relative ductility and tensile strength of the screen and the ductile iron, the screen may impart desirable strength to the pressed or rolled sheet.

Preferably, the deposited iron completely transfixes the screen without trace of any seam or interphase line. The total amount of impurities contained therein prior to annealing usually does not exceed 0.5%, and very rarely, 1%. These impurities consist mainly of occluded electrolyte salts, hydrogen gas and oxygen in the form of iron oxide. In the ensuing annealing treatment in the presence of reducing gases, however, these impurities are eliminated and the final product is of extreme purity, up to from 99.98% to 99.99% pure, with only traces of impurities, such as carbon, phosphorus, silica, manganese, sulphur, etc. Other forms of iron, i. e., those obtained by normal smelting processes and which are poured, are higher in these latter impurities, and exhibit crystalline patterns clearly distinguishable from that of the electrolytic iron deposited on our open-work pattern cathode.

If it is desired to make a very pure iron powder from a deposit of brittle iron produced in accordance with our invention, one can avoid contamination by particles of the embedded cathode material by making the open-work pattern of a non-magnetic or far less magnetic substance than the deposited iron. In that case, after the iron deposit and embedded pattern have been pulverized, one can readily separate the powder from the particles of the pattern by a magnetic process. Other details are likewise subject to considerable modification and variation. Thus, one may employ solutions of ferrous sulphate or other iron salts in place of ferrous chloride as the electrolyte. The kind of open-work pattern and the type of cell may be varied; so also the supporting frame and the means of insuring proper distribution of the current to the open-work pattern. The pattern may be grooved or crimped to increase its resiliency and elasticity and can then more easily

be held relatively taut within the supporting frame. Such variations and many more will be apparent to those skilled in the art.

We claim:

1. A method for the preparation of metallic powders which comprises electrolytically depositing a brittle metal upon a thin, resilient and elastic, open-work pattern composed of an electrically conductive metal, in which the total of the projected areas of the openings constitutes from 15% to 90% of the projected area of the pattern, said openings not exceeding 0.5 inch in width, until the metal deposited upon the pattern has completely filled the openings in the pattern and has formed a substantially homogeneous slab having the pattern embedded therein substantially midway between its major surfaces, and then pulverizing the metal deposit and pattern without prior separation.

2. A method for the preparation of iron powder which comprises electrolytically depositing brittle iron upon a thin, resilient and elastic, open-work pattern composed of iron in which the total of the projected areas of the openings constitutes from 40% to 80% of the projected area of the pattern, said openings not exceeding 0.5 inch in width, the said pattern being supported within a rigid, electrically conductive frame, continuing said deposition until the metal deposited upon the pattern has completely filled the openings in the pattern and has formed a substantially homogeneous slab having the pattern embedded therein substantially midway between its major surfaces, removing said metal deposit and pattern from the frame and then pulverizing the deposit and pattern without prior separation.

3. A method for the preparation of iron powder which comprises electrolytically depositing iron at temperatures below 60° C. upon a screen of between 2 and 40 mesh, composed of iron wire of from 0.001 to 0.10 inch diameter, the said screen being supported within a rigid, electrically

conductive frame, until the iron deposited on the screen has completely filled the openings in the pattern and has formed a substantially homogeneous slab having the pattern embedded therein substantially midway between its major surfaces, removing said iron deposit and screen from said frame and then pulverizing the deposit and screen without prior separation.

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