Our invention has to do particularly with iron and steel articles destined to receive vitreous enamel coatings.

This application is a continuation in part of our application Ser. No. 576,472, filed Nov. 16, 1931, for Metal articles for coating.

Enamelware is usually fabricated from iron and steel sheets produced in rolling mills. At present the usual procedure to prepare the rolled sheets for enameling is as follows: The sheets, having been rolled, cut to size and heat treated, are pickled in acid to remove scale and dirt, are washed and dried, and finally are cold rolled for temper and flatness. The acid employed in this pickling operation is usually hot sulphuric acid, or hydrochloric acid, a so-called inhibitor being usually added to the acid to avoid any excessive attack of the metal after the scale is removed in the bath. The sheets thus prepared are then shipped to fabricating plants where they are stamped or otherwise formed and brought into the desired shape ready for enameling. Before the enamel is applied, the shaped articles may be cleaned to remove any dirt, oil or other foreign matter, and finally may be pickled to remove rust. In this pickling operation usually hot sulphuric or cold hydrochloric acid is used.

Articles thus cleaned are then dipped in or sprayed with the enamel coating mass, dried and “fired”. During the firing, the enamel coating mass fuses, forming a bond with the heating base metal.

Pickling steps, as practiced upon metal sheets or articles, have for their object the lifting and removal of scale, oxide or rust, and foreign matter. This pickling of metal with acid frequently produces a certain roughness on the surface of the metal. However, the acids employed commercially have heretofore been hydrochloric or sulphuric acid in almost all cases, and a sheet when pickled in these acids and viewed under the microscope may show numerous small pits, which are not defined by sharp edges, but on the contrary are more or less rounded and shallow indentations above referred to. It is one of the principal objects of our invention to produce such an improved roughened surface.

We have found that a surface, characterized by deep and sharp edged pits, can be produced by etching with nitric acid, or an etching agent having a similar action as hereinafter explained.

In actual practice good results have been obtained by a procedure as follows: Iron or steel sheets, from which the adhering mill scale had previously been removed by pickling in hot sulphuric acid, were submerged for 40 seconds in 8% nitric acid solution at room temperature. Thereafter the sheets were scrubbed under running water, then neutralized with hot 2% tri-sodium phosphate solution and finally dried by means of hot circulating air.

The concentration of the nitric acid and the time duration of the etching may be varied to suit conditions. If desired, the nitric acid may be used hot instead of cold; practically, the cold nitric acid appears to be preferable because of the greater ease of handling and the avoidance of fumes. The same or like results may be obtained by a variety of treatments in which the metal is subjected to a bath containing an oxidizing agent and an acid in the presence of a ferrous salt, whereby ferric salts are produced in situ which seem to be the effective etching agent. The bath should contain sufficient acid to prevent hydrolysis, say, e.g., 5% of the stronger acids such as H₂SO₄ or HCl. We may also start out with such a solution containing both ferric and ferrous salts.

The oxidizing agent may consist of chlorates or nitrates or other oxygen liberating compounds or possibly gaseous oxygen bubbled through the solution, or otherwise contacted with it. Ferric salts may be produced by the action of nitric acids, chlorates, chromates or other oxidizing agents or ferrous salts, the fundamental condition required being that a sufficient concentration of an oxidizing agent be maintained in the presence of moderate concentrations of an acid to maintain concentrations of ferric salts in the neighborhood of 5%, or greater.

We have used successfully a solution having concentrations of less than 2–3% sodium chlorate in the presence of about 4% of sulphuric acid, at a temperature of 160° F. Also any method of oxidizing ferrous sulphate or ferrous chloride producing proper concentrations of ferric salts, at a temperature in the neighborhood of 160° F., will give the desired type of surface etching. The sodium chlorate example given above, after it has been in use, loses the concentrations set forth above, but the iron salts present have the same action as a starting reagent. Thus we have used an etching bath of 20% of ferric chloride, 55...
or thereabouts, with success. We have also used solutions such as ones containing 5% and 2% HNO₃.

The time factor is of importance mainly from the point of view of metal loss, and naturally no longer exposure to the etchant is necessary after the typical surface is produced.

The etching which we refer to is one in which the iron or steel is dissolved preferentially along the crystallographic planes within the grains. The crystal planes are normally different for each grain, and the treatment thus results in developing a multitude of planar surfaces at an angle to the surface of the metal. Consequently there are a multitude of tiny pits with sharp edged walls.

The type of etching to which we refer has been used by metallographers in study of crystallization habits of iron and steels, prior to the development of the X-ray for this purpose. So far as we are advised, any solution which has been employed to attack the iron grains preferentially along the crystal planes within the grains will serve our purpose, although for economy there we have mentioned or generally outlined are the ones best suited so far as we know.

We have termed the etching “crystallographic” for the above reason.

After the etching has been finished, it is necessary to thoroughly clean and neutralize the surface of the sheet. We have with success scrubbed the sheets under running water and then neutralized with 2% tri-sodium phosphate solution followed by artificial drying. Normally a black scum will be left on the metal by the etching unless thorough scrubbing and neutralizing is practiced.

We find that it is of advantage in removing this scum to treat the sheet with a dilute solution of sodium nitrate in sulphuric acid, such, for example, as a solution of 4 to 5% H₂SO₄ and 2 to 4% NaNO₃ at room temperature for five minutes. Changes in concentration and temperature will permit a shortening of time even to the extent of using a spray. If desired a weak solution of HNO₃ may be used instead.

The black scum is attacked by the solution and the subsequent scrubbing gives a bright silvery matt surface. The scrubbing must be applied immediately and artificial drying quickly applied also.

We have further found that this surface is very permanent, due probably to the covering of the surface with a thin film of oxide not visible, but lessening the susceptibility of the surface to oxidation.

The etching may be done at the plant of the sheet manufacturer or at the plant of the enameler, and may be done before or after forming the product in the desired shape. Thus in the claims that follow, when we refer to an article, we mean either a sheet, strip or a formed article.

Incident to the use of nitrate sulphuric solution in the cleaning process, we obtain an enameling sheet which does not require further picking prior to enameling. This is a great advantage commercially. We know of no enameling sheet with a proper bonding surface which will not become oxidized and not require further picking before enameling. By our invention we produce such a product.

The advantages obtained by our novel method of roughening the surface of metal to be enamelled, and in the product thereof, are of great importance. Among other advantages, our invention substantially entirely eliminates the phenomenon known to enamlers as “fish-scaling”, due, we believe, to the superior bond brought about by the deep sharp edged pits in the surface of the metal. Since fish-scaling is characterized by chipping off of particles of the enamel, it is evident that the enamled articles on which fish-scaling occurs are valueless because this defect cannot be corrected by subsequent coatings. The elimination of fish-scaling thus effects tremendous savings in the manufacture of enamled articles. It will, of course, be understood that the causes of fish-scaling are various, but the improper surface of the metal appears to be the chief cause of this defect; and so far as our experience extends, our invention has completely eliminated the trouble.

Another great advantage of our invention is realized in the use of white enamels. Those skilled in the art know that in producing white enameware usually three coatings of enamel are required, the first coating adjacent the metal usually being a dark ground coating. The darkness of the ground coating with certain agents, such as cobalt or nickel compounds, which are more or less indispensable as admixtures to the enamel mass at the present state of the art, for the production of a satisfactory initial bond, such compounds being of such a dark color that they darken the coating, though used in small amounts. If on such a dark ground coat only one white coat is applied, the finished enamelled article will not have a true white appearance, since it is impossible to apply a white coat of sufficient thickness and opacity to prevent the dark ground coat from showing through. This results in a coloring usually referred to by those skilled in the art as a “skimmed milk” coloring. Therefore, an additional white coat must be applied to the first white coat, resulting in three coating operations.

Hitherto it has not been possible to eliminate the second white coat by using a so-called white-grey ground coat which does not contain cobalt or nickel compounds, because such a ground coat does not have as good bonding qualities, and leads to fish-scaling and other defects of the product. Hence, such light ground coats have not been adopted by the trade in the manufacture of high grade white enameware.

It is an extremely valuable advantage of the novel sheet produced in accordance with our invention that white-grey ground coats give an excellent bond therewith, due to the deep, sharp edged pits in its surface. It has been found that by using the novel enameling sheet, first class white enameware can be produced by only two coats: namely, a white-grey ground coat and one white coat, thus eliminating entirely the second white coat.

Another advantage of our invention is that, due to the deep, sharp edged pits on the surface of the metal, the liquid enamel mass drains more uniformly and permits a greater variation in the enamel “set-up.” The term “set-up” is well known to enamlers and has to do with the admixture of certain elements with the enamel coating mass, such as clay, borax and water. While the percentage of clay used is usually constant, the percentage of borax and water may be varied to provide a certain consistency controlling the thickness of the resulting coating.

The enameler, if he cleans the sheets with the usual pickel after forming, need not destroy the typical surface produced by our invention.
There is an important distinction between pickling as such, and etching. A pickling is a treatment essentially for lifting the scale or foreign matter from a sheet or article. It is primarily a cleaning step, though the chemical action may result in some incidental, and usually undesirable, pitting. Our etching is a deliberate treatment for the purpose of giving a new surface to a sheet or article, and in our invention is a treatment for the production of such a pitting therein as will form a tooth upon said surface.

While our invention is not restricted to the treatment of cleaned and pickled sheets, yet we prefer to treat such sheets, since then we secure a desirable uniformity of pitting, which is not so readily possible in a combination pickling and etching treatment, where the irregular or spotty adherence of scale or foreign matter retards the chemical action in certain areas.

If a sheet pickled according to previous practice in hydrochloric or sulphuric acid be compared under the microscope with a sheet etched according to our invention, the difference will be unmistakable. The deep, sharp edged pits produced by our invention give a velvety or matted-like appearance to the metal which is easily recognized, and in no way similar to the surface produced by the usual pickling solutions.

While this invention has been described as applied to vitreous enameling, it is not inherently limited thereto, since the adherence of other coatings on metal are also improved by a tooth produced in accordance with this invention, e.g. baked enamels, lacquers and other paints.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent, is:

1. An iron or steel article suitable for the reception of vitreous enamel, the surface of which is characterized by deep pits bounded by sharp edged portions and planar type side walls, which is substantially identical with the crystallographic surface produced when an iron or steel article is submerged for forty seconds in eight percent nitric acid solution at room temperature.

2. An article as claimed in claim 1, the surface of which has been passivated.

3. That process of coating iron or steel articles with vitreous enamel, which comprises etching the surfaces thereof so as to produce therein closely spaced, deep, sharp edged pits, the bounding surfaces of which follow crystallographic planes in the metal itself substantially identical with those produced by submerging an iron or steel article for forty seconds in eight percent nitric acid solution at room temperature, immediately cleaning, neutralizing and drying the etched surface and afterward applying a vitreous enamel to the surface so prepared.

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