PROCESS AND COMPOSITION FOR ETCHING FERROUS METAL SURFACES

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9 Claims

ABSTRACT OF THE DISCLOSURE

A dry powder composition upon addition to water provides an acid bath for etching ferrous surfaces and consists essentially of urea nitrate, a water-soluble auxiliary dry acidic component and optionally a finely divided inert filler. The acidic components may be organic or inorganic acids or the acid salts thereof but do not include reducing agents or film forming radicals.

The present invention relates to the chemical etching of metals, and more particularly, to a method for etching ferrous surfaces and to a powder composition for preparing the bath therefor.

Methods and compositions for etching steels and various other metals are, of course, old in the art. In many cases, however, the rates of attack of the available etchants are not readily controlled. Moreover, it is often difficult to obtain a desirable degree of uniformity in etching. Generally, the etchant employed for ferrous surfaces is nitric acid and the liquid acid employed creates dangerous and otherwise undesirable working conditions.

Accordingly, it is an object of the present invention to provide a process for etching ferrous metal surfaces at a controlled rate and in a manner that will give substantially uniformly etched surfaces.

It is also an object to provide a self-contained dry powder formulation which, upon addition to water, will produce a highly effective bath for the chemical etching of ferrous surfaces and which is convenient and safe to ship and handle, relatively economical in operation and precontrolled in the optimum proportion of essential ingredients so as to provide a balanced bath composition.

Another object is to provide such a self-contained dry powder formulation which can be used at any rate of attack upon the metal workpieces can be readily varied by varying the amount of powder formulation added to water and/or the temperature.

It has now been found that the foregoing and related objects can be readily attained by use of a self-contained dry powder composition comprising urea nitrate and dry, auxiliary acidic component. The components and their concentrations are carefully selected so that upon solution of the prepared powder in a suitable quantity of water, a bath will result having a pH of about 0.2 to 2.0 which will etch ferrous surfaces substantially uniformly. In addition to urea nitrate and the auxiliary acidic composition, a powdering or anti-caking agent, and possibly other additives, are beneficially included in the powder. The bath formed by the dissolved composition may be used at ambient and elevated temperatures, i.e., about 60 to 150° Fahrenheit, with the time of immersion necessary for etching the workpiece varying with the concentration and temperature of the bath.

More particularly, the powder compositions of the present invention comprise 80.0 to 95.0 percent, and preferably 85.0 to 90.0 percent, by weight of urea nitrate. Accordingly, the dry, auxiliary acidic component comprises 5.0 to 20.0 percent by weight, and preferably 10.0 to 15.0 percent by weight, of the composition.

Although the theory of operation is not understood, it is believed that the urea nitrate provides a controlled source of nitric acid for the bath and that the urea exerts some surface activity enhancing the etching activity. At higher concentrations and elevated temperatures with certain alloys, the urea nitrate acts to substantially eliminate fuming. The auxiliary acidic component contributes to the controlled etching activity and appears to improve the surface appearance while facilitating shipment of the composition as a desirably dry composition which is readily soluble in water. It is possible that the auxiliary acidic compounds tie up certain deleterious ions which occur in the solution. It is thought that, for example, ferrous ions which are produced as a natural consequence of the etching process are tied up by the sequestering of chelating action of certain of the compounds such as the gluconic acids.

To be suitable, the auxiliary acidic component not only must be acidic, in the sense of the Lewis acid-base theory, but it must, of course, also be dry and water-soluble. Moreover, it must not be an active reducing agent and should not include a film-forming radical (i.e. phosphate and chromate radical-containing compounds are unsuitable as the second component). Accordingly, various compounds may be employed as the acidic component such as the dry acids exemplified by boric, tartaric, malic, citric, succinic and amonic acids. In addition to acids per se, numerous acidic salts can also be utilized exemplified by acidic tartrates and sulfates of the alkaline metal, alkaline earth metals and ammonia. The bisulfates are particularly advantageous in that they aid in the control of pH in the solution. Other compounds which are particularly suitable are those which conform to the above criteria and are also chelating or sequestering agents. Exemplary of such compounds are gluconic acid and particularly the delta-lactone thereof.

In addition to the urea nitrate and the dry acidic component, as was mentioned above, other components may also be advantageously included in the powder compositions. One such component is a powdering, or anti-caking, agent which is a finely divided inert filler such as a finely divided calcium silicate. When employed, such a powdering agent is advantageously included in an amount within the range of 0.5 to 5.0 percent based on the weight of powder. The admixture of other components such as surfactants, etc., which will occur to those skilled in the art is also within the scope of the present invention.

Thus, one of the preferred compositions in accordance with the present invention is composed of about 84.6 percent by weight of urea nitrate, about 8.7 percent by weight of boric acid, about 4.75 percent by weight of ammonium acetate and about 1.95 percent by weight of powdering agent. A second preferred composition comprises a quantity of urea nitrate and Micro-Cell E similar to the above, but includes the delta-lactone of gluconic acid in lieu of the boric acid and ammonium acetate.

The etching solutions may be prepared in any suitable manner, one of the outstanding advantages of the present invention being that the dry composition need only be dissolved in water at the point of utilization to produce the etchant. Hence, the desired components are premixed in precise ratios at the point of manufacture where quality control is most effectively maintained, leaving only the most rudimentary measurements to be carried out by the ultimate operator who need not be especially skilled to achieve desirable results. The bath may be readily replenished merely by addition of the powder formulation to again obtain a high degree of desirable etching activity.

Since the water is added by the ultimate operator, the utilization is dry during transit. This not only decreases the expense of transportation by keeping the weight to a minimum, but it also facilitates packaging and handling.
at all stages. The working solution will be prepared in any suitable manner by dissolving the prepared powder in a suitable quantity of water. An amount of powder ranging from about 3.0 to 15.0 percent, and preferably from about 4.0 to 10.0 percent, by weight on the basis of the water has been found to yield etchants of the proper pH which provide high-quality surfaces. The quantity of powder composition which can be dissolved is dependent upon the temperature of the water so that the higher concentrations require elevated temperatures.

Although it is possible to employ baths of the present invention which have pH values near 2.0, it is preferred that the pH of the etchant be less than 1.0, and most desirably at about 0.6. Thus, while the operable range of pH values is from about 0.2 to 2.0, the preferred range is from 0.5 to 1.0. The pH of the solution is, of course, determined by the components of the dry powder and the concentration of powder in the solution.

As is indicated above, the present compositions and the process employing same are suitable for the etching of ferrous surfaces. The term “ferrous surfaces” as used herein refers to surfaces of iron and ferrous alloy articles and other metallic articles having a coating of iron or ferrous alloy produced by any means. Thus, the various steel alloys are included. It is to be pointed out, however, that the so-called “nitric acid-passivated metals” such as stainless steel are not well suited for etching in accordance with the present invention. Passivation is due, it is believed, to the generation of an oxide film on the surface of the metal which interferes with the etching reaction. It is hypothesized that the reaction by which such an oxide film is generated in the presence of nitrate ion is catalyzed by chromium or nickel so that passivable metals should not be utilized in baths of the present invention.

The instant process may be effectively carried out by a relatively simple series of steps. Preliminary to the etching operation, it is usually desirable, and sometimes essential, that the surface of the article to be etched be freed of dirt, oil, grease and other contaminants which might tend to interfere with the etching process or otherwise reduce the desirability of the surface of the product obtained. Methods for such cleaning operations are well known in the art. Having cleaned and, normally, dried the workpiece, it is then immersed in a solution previously prepared from a powder formulation as discussed above, the solution having a proper pH value and being maintained at a suitable temperature. Although it is not essential, it is usually desirable to provide agitation in the etching bath or to the workpiece so that a uniformly etched product is obtained. After a short time, the article is removed from the etchant and subjected to subsequent treatments which may include rinsing and neutralization steps. Solutions of compounds such as sodium hydroxide and sodium cyanide are suitable for the neutralization step when it is employed, sodium cyanide being a particularly useful neutralizer since it also provides some corrosion protection to the etched surface. Other salts, such as those of potassium, can be similarly utilized. As an additional subsequent step, it is frequently desirable to desmut the surface of the article such as with an anodic alkaline technique. This is particularly true when plating of the surface is contemplated. The composition of the smut, which is in many cases believed to be a carbide, will depend upon the components of a particular alloy. Oxidizing washes tend to stain the etched surfaces and should, therefore, be avoided.

Exemplary of the efficacy of the present invention are the following specific examples wherein baths were prepared by addition of water of dry powder compositions in accordance with the present invention.

**Example 1**

A dry powder formulation is prepared containing by weight 84.6 percent urea nitrate, 8.7 percent boric acid, 4.75 percent ammonium acetate, and 1.95 percent of finely divided calcium silicate.

Into 1.5 liter of water at ambient temperature is dissolved 90.0 grams of the above powder formulation to produce an acid bath having a pH measured at 0.6. Hull cell panels (zinc-plated steel) 25% inches in diameter were previously prepared by stripping the zinc with hydrochloric acid, rinsing, treating with sodium nitrite to prevent rusting, desmutting, drying and weighing them. Ten such panels were immersed in the etchant which was at ambient temperature. After immersion in the agitated bath for about two minutes, the panels were withdrawn from the solution, rinsed with water and weighed. All panels were observed to be uniformly etched with highly desirable dull-matte finishes.

A second group of ten panels was treated with the same solution in the above-described manner. They were observed to have equally well-etched surfaces.

Third and fourth batches were also sequentially etched in the same bath. The quality of etch on these panels was observed to be somewhat lower than that of the panels in the first two replicates. Therefore, an additional charge of 90.0 grams of powder was added to the bath.

Three replicates of ten panels each were subjected to etching in the thus-rejuvenated bath under conditions similar to those which were employed with previous replicates. The first group of panels subjected to the rejuvenated bath had surfaces which were equally as well etched as the original two batches of panels. Thereafter, the quality of etch began to diminish in the two subsequent replicates.

An additional charge of 90.0 grams was accordingly added, followed by two replicates of ten panels each. Thereafter, the bath was again rejuvenated with 90.0 grams of powder and three replicates of panels were etched. The solution was rejuvenated twice more with 90.0 gram charges, the solubility thereof in the solution at ambient temperature being exceeded upon the addition of the final charge.

In all cases of the first replicate after rejuvenation of the bath, the quality of the etched surfaces obtained was good. The data obtained from these tests are summarized in the table which follows, which indicates the average weight loss per panel as a result of each etching, the points of addition of rejuvenating charge and panel appearance for each group of panels. In the table, a rating of A indicates good etching and panel appearance. Panels rated B exhibited somewhat less etching at the center than at the edges. Those rated C were poorly etched in the center and slightly etched near the edges. The D-rated panels were classified as poorly etched.

**Example 2**

Test similar to that of Example 1 was performed. In this test, however, the dry powder was composed of 89.0 percent of urea nitrate, 1.0 percent of the powdering agent and 10.0 percent of the delta-factone of gluconic acid. The etched panels which were obtained with the thus-modified formulation exhibited surfaces more finely

<table>
<thead>
<tr>
<th>Batch</th>
<th>Average weight loss per panel (g)</th>
<th>Additional grams of powder added to 1.5 liters of bath</th>
<th>Panel appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.23</td>
<td>0</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>0.23</td>
<td>0.22</td>
<td>A</td>
</tr>
<tr>
<td>3</td>
<td>0.14</td>
<td>0.22</td>
<td>A</td>
</tr>
<tr>
<td>4</td>
<td>0.14</td>
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<td>A</td>
</tr>
<tr>
<td>5</td>
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<tr>
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<td></td>
<td></td>
<td>0.22</td>
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</tr>
</tbody>
</table>

1 Solubility of solution exceeded.
and even more uniformly etched than those obtained with
the formulation of Example 1.

Example 3
An etching composition was prepared as in Example 1,
the powder composition containing 89.0 percent urea
nitrate, 1.0 percent of powdering agent and 10.0 percent of
codium bisulfate, all by weight. Panels obtained from
an etching operation, carried out in substantial accord-
ance with the procedure of Example 1 exhibited etched
surfaces comparable in quality to those obtained in that
example.

The temperatures and times employed in the etching
process of the present invention are generally interdepend-
ent and dependent upon the concentrations of the active
agents of the solution and also upon the desired degree
of etching. It is highly advantageous to operate the present
process with the solution maintained at ambient tempera-
ture; i.e., 60 to 100° Fahrenheit. This is, of course, the
most economical and convenient temperature, and also
one at which well-etched products are obtained. A more
rapid reaction can generally be effected by raising the
temperature of the solution. This in itself will serve not
only to increase the rate of reaction, but it will also increase
the solubility of the powdered components in water and
thereby make possible a more concentrated and, hence,
an even more active, solution. Surprisingly, the activity
of baths containing the delta-lactone of gluconic acid was
found not to increase appreciably with elevated tempera-
tures. Although higher temperatures are feasible, tem-
peratures of about 150° Fahrenheit are generally most
advantageous; temperatures in the range of 60 to 100°
Fahrenheit are preferred.
The period of immersion can vary within wide limits,
times of from about ten seconds to about ten minutes
being feasible and of one to five minutes being preferred.
While an increased degree of control is obtained when
the reaction is slow, by virtue of a dilute solution and/or
a low temperature, it is often more economical and effi-
cient to minimize the time necessary to carry out an etch-
ing cycle. In the present process, balancing of such
considerations is a convenient and facile matter.
Since the baths are somewhat corrosive, the tanks
and handling equipment should be fabricated from acid-
resistant material, such as rigid polyvinyl chloride or a
glass cloth-reinforced resin, to avoid contamination.
The dry powder formulations are not in themselves corrosive,
but should be transported in suitable containers that will
minimize the likelihood of inadvertent contact with water
or excessive amounts of moisture.
As is seen from Example 1, replenishment of the baths
of the present invention is a simple matter which can be
affected so as to avoid the need for discarding of the
used baths at frequent intervals. The limit of replenish-
ment occurs only after multiple replenishment and build-
up of ions in the bath makes further replenishment no
longer feasible.
Thus, it can be seen that the present invention provides
a process of etching ferrous surfaces at a controlled rate
and in a manner which produces substantially uniformly
etched surfaces. The self-contained dry powders provided
by the invention produce, upon addition to water, baths
which chemically etch ferrous surfaces in a highly effec-
tive manner. The powders are convenient and safe to
handle and are economical in operation. Their nature
is such that the optimum proportions of essential ingredi-
ents of the baths are precontrolled and the rate of attack
of metal surfaces is readily varied by varying the
amount of the powder formulations added to the water.
Having thus described the invention, we claim:
1. A dry powder composition for addition to water to
provide an acid bath for etching ferrous surfaces consist-
ing essentially of 80.0 to 95.0 percent by weight of urea
nitrate, 20.0 to 50.0 percent by weight of an auxiliary water-
soluble dry acid component selected from the group
consisting of organic and inorganic acids and the acidic
salts thereof and up to 5.0 percent of a finely divided inert
filler, said dry powder composition providing a pH of
about 0.2 to 2.0 when added to water in a quantity
ranging from about 3.0 to 15.0 percent based on the weight
of water, said acidic component excluding active reducing
agents and film forming radicals.
2. The dry powder composition in accordance with
claim 1 wherein said auxiliary acid component consist-
ing essentially of a mixture of boric acid and ammonium
acetate.
3. The dry powder composition in accordance with
claim 1 wherein said auxiliary acid component addition-
ally includes a sequestering agent of acidic nature.
4. The dry powder composition in accordance with
claim 3 wherein said sequestering agent is the delta-lactone
of gluconic acid.
5. In an etching process, the steps comprising dissolv-
ing in water from about 3.0 to 15.0 percent by weight,
based upon the water, of a self-contained dry powder com-
position consisting essentially of about 80.0 to 95.0 per-
cent by weight of urea nitrate, about 20.0 to 5.0 percent
by weight of an auxiliary water-soluble dry acid com-
ponent selected from the group consisting of organic and
inorganic acids and the acidic salts thereof and up to 5.0
percent of a finely divided inert filler to prepare a bath
having a pH ranging from about 0.2 to 2.0, said acidic
component excluding active reducing agents and film form-
ning radicals; and immersing a workpiece having a ferrous
surface in said bath maintained at a temperature from
about 60 to 150° Fahrenheit for a period of time suffi-
cient to etch said ferrous surface substantially uniformly.
6. The process in accordance with claim 5 wherein said
period of time ranges from about ten seconds to ten
minutes.
7. The process in accordance with claim 5 wherein 4
to 10 parts by weight of said self-contained dry powder
composition is dissolved in 100 parts by weight of water
to prepare a solution having a pH of about 0.5 to 1.0, said
self-contained dry powder composition consisting es-
tentially of about 85 to 90 percent by weight of urea nitrate,
5.0 to 14.5 percent by weight of an auxiliary acid component
consisting essentially of boric acid and ammonium acetate,
and 0.5 to 5.0 percent by weight of finely divided inert
filler, said solution being maintained at ambient tempera-
ture and said period of time of immersion of said work-
piece being about one to five minutes.
8. The process in accordance with claim 5 wherein 4
to 10 parts by weight of said self-contained dry powder
composition is dissolved in 100 parts by weight of water,
said self-contained dry powder composition consisting es-
tentially of 85 to 90 percent by weight of urea nitrate,
0.5 to 5.0 percent by weight of a finely divided inert filler,
and 5.0 to 14.5 percent by weight of the delta-lactone of
gluconic acid.
9. The process in accordance with claim 5 wherein said
workpiece is removed from said bath and rinsed in an
aqueous cyanide bath.

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