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# ETCHING BATH FOR CORROSION AND HEAT RESISTANT ALLOYS AND PROCESS OF ETCHING

Walter L. Acker, Wethersfield, and Lloyd H. Curkin, Manchester, Conn., assignors to United Aircraft Corporation, East Hartford, Conn., a corporation of Delaware

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The present invention relates to a novel and improved etching or mordant composition especially useful in connection with high-alloy corrosion and heat resistant steels and a process of etching or chemical-milling such metals.

Objects and advantages of the invention will be set forth in part hereinafter and in part will be obvious herefrom, or may be learned by practice with the invention, the same being realized and attained by means of the compositions, processes and steps pointed out in the appended claims.

The invention consists in the novel compositions, processes, steps and improvements herein shown and described.

The present invention has for its object the provision of a novel and improved process for the etching or chemical-milling of corrosion and heat resistant steels. A further object is the provision of a novel and improved mordant composition which acts rapidly on the corrosion and heat resistant steel and which does not cause any substantial embrittlement of the metal or alloy. Still another object is the provision of a novel and improved mordant and process for use with corrosion and heat resistant steels which acts rapidly on the steels, and leaves the etched steel with an excellent surface finish.

In accordance with the composition of the present invention, the mordant comprises an aqueous solution of concentrated hydrochloric and nitric acids, in certain proportions together with ferric chloride and a surface active, wetting agent which is relatively stable in the acid solution. This mordant may be used with suitable resists, such as resinous resists or bees-wax, for the chemical-milling or etching or a wide variety of corrosion and heat resistant steels, the etching or chemical-milling being controlled by means of a suitable resist or stopping-out material.

Referring now in detail to the composition of matter which forms a part of the present invention, the mordant or etching bath comprises an aqueous solution of certain proportions of concentrated hydrochloric acid, concentrated nitric acid, ferric chloride and a wetting agent, preferably a sulfated fatty alcohol or a sodium alkyl sulfate, which is relatively stable in the mordant and is not rapidly decomposed by the nitric and hydrochloric acids present in the mordant bath.

The preferred mordant or etching bath of the present invention is prepared in accordance with the following general formula, and consists essentially of:



| | (Weight percent) |
|---|---|
| Hydrochloric acid content | 25% to 30½%, preferably 26%. |
| Nitric acid content | 9½% to 16%, preferably 12%. |
| Ferric chloride ($6H_2O$) | 0.15% to 1.0%, preferably ½%. |
| Wetting agent | 0.0015% to 0.08%, preferably 0.04%. |
| Water | Enough to make 100%. |

Such a bath is conveniently prepared by adding from four to eight parts by volume (preferably five parts) of concentrated (33%) hydrochloric acid to one part by volume of concentrated (69%) nitric acid, mixing, and adding to each liter of the mixed acids from about one-half to two ounces avdp. (preferably about 2 oz.) of ferric chloride, and from 0.005 to 0.025 oz., and preferably about 0.013 oz. of a stable wetting agent such as "Orvus W.A. Paste," or less preferably "Petrowet W.N." (Orvus W.A. Paste is a sulfated fatty alcohol and Petrowet W.N. is a sodium alkyl sulfate.)

Etching baths of the kind described which contain less than about 4 parts by volume of concentrated hydrochloric acid for each volume of concentrated nitric acid work too fast, and 5 parts of hydrochloric acid for one volume of nitric acid gives a superior surface finish to the etched parts than the 4 to 1 ratio bath.

Increasing the hydrochloric/nitric acid ratio slows down the etching speed of the bath, and when an 8 to 1 ratio is exceeded, the bath works too slowly on corrosion and heat resistant steels to be commercially useful.

Increasing or decreasing the strength of the acids used will also influence the character and speed of etching, but the etching bath is operative within the percentage compositions given above.

Reducing the concentration of the wetting agent much below 0.0015% results in a poorer surface finish. Increasing the wetting agent concentration above about 0.08% causes excessive foaming of the etching bath, and is objectionable from that point of view.

The mordant or etching baths of the present invention are primarily for use in the etching or chemical milling of the corrosion and heat resistant steel designated as A.M.S. 5525 having the following approximate analysis:

| | Percent |
|---|---|
| Cromium | 15 |
| Nickel | 25 |
| Molybdenum | 1.3 |
| Vanadium | 0.3 |
| Titanium | 2.0 |
| Aluminum | 0.2 |
| Carbon | 0.08 |
| Iron | Remainder |

but has also been found to be useful in connection with

| AMS | Fe | C | Mn | Si | P | S | Cr | Ni | Mo | Al | Cu | Sn | Cb and Ta | V | W | Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5504 | (1) | [2].15 | [2]1.00 | [2]1.00 | [2].04 | [2].03 | 11.5–13.5 | [2].75 | [2].50 | [2].05 | [2].50 | [2].05 | | | | |
| 5512 | (1) | [2].08 | [2]2.00 | .50–1.00 | [2].04 | [2].03 | 17–19 | 9–12 | [2].50 | | | | 10%C [2]1.10 | | | |
| 5521 | (1) | [2].08 | [2]2.00 | [2].75 | [2].04 | [2].03 | 24–26 | 19–22 | [2].50 | | [2].50 | | | | | |
| 5524 | (1) | [2].08 | [2]2.00 | [2]1.00 | [2].04 | [2].03 | 17–19 | 12–14 | 2–3 | | [2].50 | | | | | |
| 5616 | (1) | .12–.17 | [2].50 | [2].50 | [2].04 | [2].03 | 12–14 | 1.8–2.2 | [2].50 | [2].15 | [2].50 | [2].05 | | | | |
| 5735 | (1) | [2].08 | 1.00–2.00 | .40–1.00 | [2].04 | [2].03 | 13.5–16 | 24–27 | 1–1.50 | [2].35 | | | | .10–.50 | 2.5–3.5 | |
| 5736 | (1) | [2].08 | 1.00–2.00 | .40–1.00 | [2].04 | [2].03 | 13.5–16 | 24–27 | 1–1.50 | [2].35 | | | | .10–.50 | | 1.75–2.25 |
| 6355 | (1) | .28–.33 | .70–.90 | .20–35 | [2].04 | [2].04 | .4–.6 | .4–.7 | .15–.25 | | | | | | | 1.75–2.25 |
| 5040 | (1) | [2].15 | .25–.60 | | [2].04 | [2].05 | | | | | | | | | | |

[1] Remainder.
[2] Maximum.

the preceding alloys; whose percentage composition is given in the table.

Concentrated hydrochloric acid alone will not deeply etch such corrosion and heat resistant steels, nor will ferric chloride and hydrochloric acid in the absence of nitric acid, nor will a mixture of ferric chloride and nitric acid, although certain of these solutions will pickle the surface of such corrosion and heat resistant steels.

With typical corrosion and heat resistant steels such as AMS No. 5525, and at etching temperatures of from 105° to 150° F. as much as 0.025" thickness of metal can be removed per hour of etching.

The corrosion and heat resistant steel to be etched or chemical-milled may be in the form of sheet, finished parts, forgings or castings, and these parts are provided with the surface coating of impervious material in those areas which are not to be etched, after which the alloy or metal is immersed in, or sprayed with, the mordant for a sufficient period of time to remove the desired amount of metal. The etching may be carried out at room or at an elevated temperature, and during the etching process, the hydrogen evolved is rapidly removed from the surface of the metal or alloy.

The chemical-milled pieces have a bright, clean surface which is relatively smooth, only slightly matted.

When the rapid action of the mordant has ceased, the bath is preferably replaced by a new bath.

The invention in its broader aspects is not limited to the specific compositions, processes and steps shown and described but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed is:

1. An etching bath for corrosion and heat resistant steel consisting essentially of by weight an aqueous solution of from 25% to 30½% of hydrochloric acid, from 9½% to 16% of nitric acid, from 0.15% to 1% of ferric chloride and from 0.0015% to 0.08% of a wetting agent stable in the presence of nitric and hydrochloric acids.

2. An etching bath consisting essentially of four to eight parts by volume of concentrated hydrochloric acid, one volume of concentrated nitric acid, from ½ to 2 oz. of ferric chloride per liter, and from 0.005 to 0.025 oz. per liter of a wetting agent selected from the group consisting of sodium alkyl sulfates and sulfated fatty alcohols.

3. An etching bath consisting of essentially of by weight an aqueous solution of 26% of hydrochloric acid. 12% of nitric acid, ½% of ferric chloride and 0.04% of a wetting agent selected from the group consisting of sodium alkyl sulfates and sulfated fatty alcohols.



4. An etching bath consisting essentially of five parts by volume of concentrated hydrochloric acid, one part by volume of concentrated nitric acid, 1 oz. of ferric chloride and 0.013 oz. per liter of a wetting agent selected from the group consisting of sodium alkyl sulfates and sulfated fatty alcohols.

5. The process of etching corrosion and heat resistant steel which comprises subjecting the steel to the etching action of a bath consisting essentially of by weight an aqueous solution of from 25% to 30½% of hydrochloric acid, from 9½% to 16% of nitric acid, from 0.15% to 1% of ferric chloride, and from 0.0015% to 0.08% of a wetting agent stable in the presence of nitric and hydrochloric acids.

6. The process of etching corrosion and heat resistant steel which comprises subjecting the steel to the etching action of a bath consisting essentially of four to eight parts by volume of concentrated hydrochloric acid, one part of concentrated nitric acid, one-half to two ounces ferric chloride per liter, and from 0.005 to 0.025 oz. per liter of a wetting agent selected from the group consisting of sodium alkyl sulfates and sulfated fatty alcohols.

7. The process of etching corrosion and heat resistant steel which comprises subjecting the steel to the etching action of a bath consisting essentially of by weight an aqueous solution of 26% of hydrochloric acid, 12% of nitric acid, ½% of ferric chloride and 0.04% of a wetting agent selected from the group consisting of sodium alkyl sulfates and sulfated fatty alcohols.

8. The process of etching corrosion and heat resistant steel which comprises subjecting the steel to the etching action of an etching bath consisting essentially of five parts by volume of hydrochloric acid, one part by volume of nitric acid, ferric chloride 1 oz. per liter and a wetting agent stable in the presence of nitric and hydrochloric acids, 0.013 oz. per liter.

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