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BATHS FOR ONE-STAGE QUICK ETCHES

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10 Claims. (Cl. 156—8)

This invention relates in general to etching baths and processes for etching devices composed of metals such as zinc and magnesium, and various alloys such as zinc and magnesium alloys, and more particularly to an improved bath and process for effecting a one-stage quick etch. This application constitutes a continuation-in-part of application for patent Ser. No. 526,783, filed August 5, 1955, now abandoned.

Among the objects of the present invention, it is aimed to provide an improved bath or bath solution and process to effect a one-stage quick etch for etching various metals such as zinc and magnesium and various alloys such as zinc alloys, magnesium alloys and the like, which solution can be produced at a minimum of cost as compared to the cost of solutions today used in baths for producing a quick etch, which solution is more stable than solutions today in use for producing a quick etch, which solution is more flexible, that is, the ingredients of which can be varied relative to one another without materially changing the end result obtainable, which solution and process is not accompanied by objectionable odor such as is the case with the solutions today used for producing a quick etch, and which one-stage quick etch can be completed in a minimum period of time.

As compared to the cost of solutions heretofore in use for effecting a one-stage quick etch which cost about double the cost of the conventional four to five stage etching baths containing only water and nitric acid, the cost of the present solution is only fifty percent more than that of the conventional four to five-stage etching bath or seventy-five percent of the earlier one-stage solution.

As compared to the stability of the solutions heretofore in use for effecting a one-stage quick etch which did not exceed eight hours, the present solution will remain effective for at least four days. In other words, the one-stage solutions today in use deteriorate by reaction of the ingredients with each other to the degree that the effect can be observed on the results produced by the solutions, even after only one hour of standing without being used. This rate of deterioration is so great that the number of engravings which can be produced using the solution is largely determined by the age of the solution. For example, a fresh solution made one day is normally considered unusable the next day and is discarded, even if it has had little or no use.

On the other hand, with the present solution, no effect of deterioration due to reaction of the ingredients with each other could be observed on the results produced by the solutions after four days of standing without use. The practical result is that the number of engravings which can be produced by the present solution is determined only by weight of metal dissolved into the solution, not by age. The economy in cost of materials and especially in time saved in not discarding relatively unused baths represents a substantial saving and increase in efficiency for the user.

In addition, the solutions today in use also deteriorate by evaporation. The present solution uses blends of aromatic and aliphatic hydrocarbon solvents with relatively low rates of evaporation.

As compared to the comparative inflexibility of solutions heretofore in use, the ingredients of the present solu-

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tion proportionately could vary as much as 10% without affecting etching efficiency.

As compared to the odor of solutions heretofore used for one-stage quick etching, the present solution is much less objectionable in odor. This odorless characteristic is of inestimable value in view of health department regulations of municipalities barring dumping of used or deteriorated solutions of this type on account of their odor.

With all of the aforesaid advantages over solutions heretofore in use, the time period for effecting an effective etching process in a one-stage quick etch with the present solution will not exceed the seven to ten minutes required for effecting a one-stage quick etch of the process heretofore in use and in turn the time period for effecting an etching process with the present solution compares extremely favorable with the forty-five to sixty minutes' time period required to effect an efficient etching process by the conventional long processes using three to five stages.

In order to produce a satisfactory bath solution and process according to the present invention it was found necessary to mix nitric acid, water, a petroleum solvent and at least one wetting agent which is an essentially solvent soluble alkyl aryl sulphonate including the acid form as well as the sodium salts of the same. An additional improvement in results is obtained by including a second wetting agent, essentially water soluble, such as water-soluble alkyl aryl sulphonates. Aside from this improvement in results, the water-soluble wetting agent also reduces the possibility of a thickening of the solution, making it unusable, which possibility exists just beyond but not within the preferred range of compositions of the bath. Basically, in addition to improving results, its secondary function is that it adds to the flexibility of permissible variations in proportions of other ingredients and variations in mechanical conditions which can be used to produce satisfactory results.

The solution so mixed is essentially a physical mixture, to wit, an emulsion, the ingredients of which do not react upon one another chemically when mixed in this four or five part group, in the interest of maintaining consistency of results obtained from the solution, without effect by the age of the solution. The petroleum solvent in this mixture was selected in the interest of reducing odor and cost of the material to a minimum and was also found to improve the results obtained.

Excellent results have been achieved when these ingredients have been used in approximately the proportions set forth in the following examples:

Example 1

Parts by weight

42 Bé. nitric acid.....	10.7
150° F. flash solvent, aromatics content 90-93%	7.9
Long chain alkyl aryl sulphonate, average molecular weight 450, average chain length of alkyl portion 18 to 24 carbon atoms.....	0.18
Alkyl aryl sulphonate average chain length (alkyl portion), 12 carbon atoms.....	0.04
Water	81.8
	100.0

Example 2

42 Bé. nitric acid.....	10.7
150° F. flash solvent, aromatics content 90-93%	7.12
Long chain alkyl aryl sulphonate, average molecular weight 450, average chain length of alkyl portion 1 to 24 carbon atoms.....	0.12
Alkyl aryl sulphonate, average chain length (alkyl portion), 12 carbon atoms.....	0.00008
Water	82.06
	100.0

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Example 3

42 Bé. nitric acid-----	11.8
150° F. flash solvent, aromatics content 90-93%-----	7.9
Long chain alkyl aryl sulphonate, average molecular weight 450, average chain length of alkyl portion 18 to 24 carbon atoms-----	0.16
Isopropyl naphthalene sulphonate-----	0.15
Water-----	80.09
	100.0

Example 4

42 Bé. nitric acid-----	13.0
150° F. flash solvent, aromatics content 90-93%-----	7.8
Long chain alkyl aryl sulphonate, average molecular weight 450, average chain length of alkyl portion 18 to 24 carbon atoms-----	0.18
Sodium N-methyl-N-oleoyl taurate-----	0.04
Water-----	78.98
	100.0

Example 5

42 Bé. nitric acid-----	11.8
150° F. flash solvent, aromatics content 90-93%-----	8.2
Long chain alkyl aryl sulphonate, average molecular weight 450, average chain length of alkyl portion 18 to 24 carbon atoms-----	0.16
Technical lauryl sodium sulphate-----	0.02
Water-----	79.82
	100.0

Example 6

42 Bé. nitric acid-----	11.8
Medium boiling range aliphatic hydrocarbon aromatics content 20%-----	7.2
Long chain alkyl aryl sulphonate, average molecular weight 450, average chain length of alkyl portion 18 to 24 carbon atoms-----	0.22
Alkyl aryl sulphonate, average chain length (alkyl portion), 12 carbon atoms-----	0.06
Water-----	80.72
	100.0

Although the water-soluble alkyl aryl sulphonate has been found particularly effective in preventing thickening of the solution, at certain concentrations of the other ingredients, good results have also been achieved when the water-soluble alkyl aryl sulphonate has been entirely omitted in the solution, as illustrated by the following example:

Example 7

	Parts by weight
42 Bé. nitric acid-----	10.7
150° F. flash solvent, aromatics content 90-93%-----	5.4
Long chain alkyl aryl sulphonate, average molecular weight 450, 18 to 24 carbon atoms-----	0.4
Water-----	83.5
	100.0

Similarly instead of omitting the water-soluble alkyl aryl sulphonate entirely, excellent results have been achieved when the water-soluble alkyl aryl sulphonate was greatly reduced, as an instance, 0.00005-0.0001 part by weight, as illustrated in Example 2.

It is to be noted that Examples 1 and 2 aforesaid recite different proportions of the same ingredients and that in particular the usable proportions of solvent and solvent-soluble wetting agent depend upon the proportion of the water-soluble alkyl aryl sulphonate present in the formula.

The specific amounts of the ingredients listed in the aforesaid seven examples may be varied without appreciably changing the results produced. As an instance, Examples 1 and 2 aforesaid may be changed as follows:

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Example 8

3-20 part nitric acid	
1-12 part petroleum solvent, containing 0-100% aromatic solvent 0-100% aliphatic solvent	
0.02-2.0 parts long chain alkyl aryl sulphonate with an average molecular weight about 450 and an average chain length of 18 to 24 carbon atoms	
0-2.0 parts alkyl aryl sulphonates, with an average alkyl chain length of about 12 carbon atoms	
Remainder of the 100 parts total being water	

Example 3 aforesaid on the other hand may be changed as follows:

Example 9

3-20 parts nitric acid	
1-12 parts petroleum solvent	
0.02-2.0 parts long chain alkyl aryl sulphonate with an average molecular weight of about 450 and an average chain length of about 18 to 24 carbon atoms in the alkyl portion	
0-2.0 parts isopropyl naphthalene sulphonate	
Remainder of the 100 parts total being water	

Example 4 aforesaid may be changed as follows:

Example 10

3-20 parts nitric acid	
1-12 parts petroleum solvent containing 0-100% aromatic solvent	
0.02-2.0 parts long chain alkyl aryl sulphonate with an average molecular weight of about 450 and an average chain length of about 18-24 carbon atoms in the alkyl portion	
0-2.0 parts of the reaction product of a fatty acid and an organic sulphonate, such as sodium-N-methyl-N-oleoyl taurate	
Remainder of the 100 parts total being water	

Example 5 aforesaid may be changed as follows:

Example 11

3-20 parts nitric acid	
1-12 parts petroleum solvent containing 0-100% aromatic solvent	
0.02-2.0 parts long chain alkyl aryl sulphonate with an average molecular weight of about 450 and an average chain length of about 18-24 carbon atoms in the alkyl portion	
0-0.1 part alkyl sulphate, such as an alkali metal-salt of lauryl sulphate	
Remainder of the 100 parts total being water	

While any of the conventional solvent-soluble alkyl aryl sulphonate wetting agents today in use could be used, excellent results have been achieved with the solvent-soluble alkyl aryl sulphonate wetting agent when it has the following physical properties, to wit: having a chain length of the alkyl portion of about 18 to 24 carbon atoms, an average molecular weight of 450, about 50 to 55% active ingredients, and about 45 to 50% free oil.

In turn, while any number of the well-known water-soluble wetting agents today in use could be used to advantage, excellent results have been achieved with the water-soluble wetting agents known in the trade as Nacconol NRSF, Aerosol OS, Igepon T-77 or Duponol ME Dry.

The typical physical properties of these four water-soluble wetting agents are as follows:

Nacconal NRSF is a medium-chain alkyl aryl sulphonate, having an average chain-length of the alkyl portion of about 12 carbon atoms, about 92% active ingredients, and the remaining 8% being essentially sodium sulphate.

Aerosol OS is a short chain alkyl aryl sulphonate consisting of about 80% isopropyl naphthalene sulphonate and the remainder being essentially sodium sulphate.

The Igepon T-77 is an example of the product of

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the reaction of a fatty acid and an organic sulphate consisting of about 72% sodium-N-methyl-N-oleoyl taurate and the remaining 28% being essentially sodium chloride.

The Duponol ME Dry is an alkyl sulphate consisting of about 90% technical lauryl sodium sulphate and the remaining 10% being essentially sodium sulphate.

While any one of the conventional petroleum-cut solvents today in use could be used, excellent results have been achieved when any of the petroleum-cut solvents known in the trade as Solvesso 150, Amsco Solv E, or Amsco 460 Solvent, was selected. The typical properties of these three petroleum-cut solvents are substantially as follows:

Properties	Solvesso 150	Amsco Solv E	Amsco 460 Solvent
API Gravity @ 60° F.	26.9	28.3	42.0
Spec. Gravity @ 60° F.	0.893	0.886	0.816
Lbs. per Gallon	7.44	7.37	6.79
Distillation:			
IBP, ° F.	367	362	362
50%, ° F.	378	406	400
Dry End Pt., ° F.	417	490	455
Final End Pt., ° F.	418	494	458
Flash Pt., ° F., Tag CC.	150	146	143
Kauri-Butanol, cc.	90	74.5	37.6
Aniline Cloud Pt., ° F.			137
Aniline Cloud Pt., ° F., mixed.	67.3	87.5	
Percent Aromatics	93	75	20

While solutions made according to the present invention can be used to good advantage in etching devices or plates composed of a great variety of metals, excellent results have been achieved with zinc and magnesium alloys. Examples of such alloys are as follows:

(A) Zinc-base alloys:

- (1) 0 to 1.0% cadmium
0 to 0.025% iron
0 to 0.05% magnesium
0 to 0.2% nickel
Remainder zinc
- (2) 0 to 1.0% aluminum
0 to 0.05% magnesium
Remainder zinc
- (3) At least 90% zinc and the
Remainder, other metals.

(B) Magnesium base alloy:

- (1) 3% aluminum
1% zinc
0.2% manganese
Remainder magnesium
- (2) At least 80% magnesium and
The remainder, other metals.

From the foregoing it will thus be seen that due to the fact that the various ingredients of the baths here disclosed merely form physical mixtures in the form of emulsions as distinguished from chemical inter-reactions the baths will remain effective for periods of at least two weeks. It has been found, as an instance, that the alkyl aryl sulphonates will not react chemically with any of the ingredients of the solution but in the etching process will form a protective film to enable the acid of the solution to penetrate the exposed portions, the depth necessary without any objectionable undercutting.

As is conventional with etching processes, the image to be formed in relief on a device is coated with an acid resisting coating and thereupon the etching mixture is supplied either by splashing, spraying or the like on the remaining exposed or unprotected faces of the device. In the present instance, the etching mixture is the mixture heretofore set forth and constituting a part of the invention.

It is obvious that various changes and modifications may be made in the ingredients and the percentages of ingredients aforesaid without departing from the general spirit of the invention as set forth in the appended claims.

We claim:

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1. A bath solution for a one-stage quick etch on an alloy comprising by weight 3 to 20 parts nitric acid, 1 to 12 parts of a petroleum solvent, 0.2 to 2.0 parts long chain alkyl aryl sulphonate, and 0.00008 to 2.0 parts alkyl aryl sulphonate having a chain length of about 3 to 12 carbon atoms, and the remainder water.

2. A bath solution for a one-stage quick etch on an alloy comprising by weight 11.8 parts nitric acid, 80.09 parts water, 7.9 parts of a petroleum-cut solvent having an aromatic content of 90 to 93%, 0.16 part long chain alkyl aryl sulphonate with a molecular weight of about 450 and a chain length of about 18 to 24 carbon atoms, and 0.15 part isopropyl naphthalene sulphonate.

3. A bath solution for a one-stage quick etch on an alloy comprising by weight 13.0 parts nitric acid, 78.98 parts water, 7.8 parts of a petroleum-cut solvent having an aromatic content of 90 to 93%, 0.18 part long chain alkyl aryl sulphonate with a molecular weight of about 450 and a chain length of about 18 to 24 carbon atoms, and 0.04 part sodium-N-methyl-N-oleoyl taurate.

4. A bath solution for a one-stage quick etch on an alloy comprising by weight 11.8 parts nitric acid, 79.82 parts water, 8.2 parts of a petroleum-cut solvent having an aromatic content of 90 to 93%, 0.16 part long chain alkyl aryl sulphonate with a molecular weight of about 450 and a chain length of about 18 to 24 carbon atoms, and 0.02 part technical lauryl sodium sulphate.

5. A bath solution for a one-stage quick etch on an alloy comprising by weight 3 to 20 parts nitric acid, 1 to 12 parts petroleum solvent, 0.02 to 2.0 parts long-chain alkyl aryl sulphonate with an average molecular weight about 450 and an average chain length of 18 to 24 carbon atoms, 0.00008 to 2.0 parts alkyl aryl sulphonate, with an average chain length of about 3 to 12 carbon atoms, and the remainder water.

6. A bath solution for a one-stage quick etch on an alloy comprising by weight 3 to 20 parts nitric acid, 1 to 12 parts petroleum solvent, 0.02 to 2.0 parts long chain alkyl aryl sulphonate with an average molecular weight of about 450 and an average chain length of about 18 to 24 carbon atoms, 2.0 or less parts isopropyl naphthalene sulphonate, and the remainder water.

7. A bath solution for a one-stage quick etch on an alloy comprising by weight 3 to 20 parts nitric acid, 1 to 12 parts petroleum solvent, containing 0 to 100% aromatic solvent, 0.02 to 2.0 parts long chain alkyl aryl sulphonate with an average molecular weight of about 450 and an average chain length of about 18 to 24 carbon atoms, 0.1 part or less alkyl sulphate, and the remainder water.

8. A bath solution for a one-stage quick etch on metal alloys comprising by weight 3 to 20 parts of nitric acid, 1 to 12 parts of a petroleum solvent, surface active agents consisting of 0.02 to 2.0 parts of a solvent soluble alkyl aryl sulphonate and 0.00008 to 2.0 parts of a wetting agent selected from the group of essentially water soluble agents consisting of alkyl aryl sulphonates, alkyl sulphates and a sulphonate resulting from the reaction of a fatty acid and an organic sulphonate, and the remainder water.

9. The process of etching a device composed of metals selected from the group consisting of zinc, magnesium, zinc base alloys and magnesium base alloys consisting in said device having portions of its surface covered with an acid resisting coating to define a design and applying an etching mixture to the remaining exposed or unprotected faces of the device with an etching mixture of between 3 to 20 parts by weight of nitric acid, of between 1 to 12 parts by weight of a petroleum solvent, surface active agents consisting of between 0.02 to 2.0 parts by weight of an oil soluble alkyl aryl sulphonate and, of between 0.00008 to 2.0 parts by weight of an essentially water soluble wetting agent, and the remainder water.

10. The process of etching a device composed of

metals selected from the group consisting of zinc, magnesium, zinc base alloys and magnesium base alloys consisting in said device having portions of its surface covered with an acid resisting coating to define a design and applying an etching mixture to the remaining exposed or unprotected faces of the device with an etching mixture of between 3 to 20 parts by weight of nitric acid, of between 1 to 12 parts by weight of a petroleum solvent, surface active agents consisting of .02 to 2.0 parts by weight of an oil soluble alkyl aryl sulphonate and of between 0.00008 to 2.0 parts by weight of a wetting agent selected from the group of essentially water soluble agents consisting of alkyl aryl sulphonates, alkyl sulphates and a sulphonate resulting from the reac-

tion of a fatty acid and an organic sulphonate and the remainder water.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,074,836

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 3, for "0.2 to 2.0 parts" read -- 0.02 to 2.0 parts --; line 16, for "petaroleum-cut" read -- petroleum-cut --.

Signed and sealed this 31st day of March 1964.

(SEAL)
Attest:

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