

1

3,728,188

## CHROME-FREE DEOXIDIZING AND DESMUTTING COMPOSITION AND METHOD

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### ABSTRACT OF THE DISCLOSURE

A deoxidizing and desmutting process, employing chrome-free compositions and providing improved solutions for treating aluminum surfaces, in preparation for subsequent finishing operations. The invention, in both its method and composition aspects, involves preventing smut formation on the deoxidized aluminum surface, controlling surface etch during the deoxidizing process, and prolonging the effective life of the aqueous acidic deoxidizing solution.

An aluminum surface is often covered with surface corrosion and an oxide film formed through atmospheric oxidation of the metal surface. Should the aluminum surface undergo a finishing treatment such as spot welding, conversion coating, anodizing or painting, the oxide film and surface corrosion must be removed. Should the oxide film be allowed to remain on the surface, it would interfere with the subsequent finishing step. For example, a subsequently applied protective coating such as an anodized coating or a chemical conversion coating, would not be uniform and would be loosely held should the oxide film be allowed to remain on the aluminum surface.

A fine particulate material, known in the art as smut, is often found on aluminum surfaces which have been treated with alkaline etching or cleaning solutions. These smut deposits are usually formed on the surface when the cleaning or etching solution reacts with the base metal. Essentially, through the attack of the base metal, the smut film is formed from residues of metals, in the form of their salts, with which the aluminum is alloyed. A desmutting operation is necessary prior to any further finishing treatment of the aluminum surface.

A variety of treatments and processes for removing the oxide film and smut deposits on aluminum surfaces are well known in the art. Such treatments and processes are disclosed, for example, in U.S. Pats. Nos. 2,883,311; 3,138,485; 3,140,203; 3,275,562; 2,353,786; 3,367,799; 3,373,114; 3,448,055; and 3,510,430.

The presence of noxious materials in the effluents of deoxidizing and desmutting baths has been a major problem. The deoxidizing solutions and processes to which reference has been made and which contain chromates, dichromates, or nitric acid, create waste disposal problems, handling problems, and difficulties due to the corrosive action of the solutions on the equipment employed. In addition, these solutions tend to contaminate the baths subsequently used in the finishing operations. When chromates or dichromates are employed, chemical treatment of the treating solutions is necessary in order to neutralize and reduce the chromate before the solutions can be discarded.

There have been attempts made in the art to remove the oxide film and smut deposits on aluminum surfaces employing processes and solutions devoid of hexavalent chromium and other highly noxious materials. For example, in U.S. Pat. No. 3,140,203 there is disclosed a chrome-free deoxidizing solution consisting of persulfate, fluoride, and a strong acid. In the disclosed solutions, the persulfate is the apparent oxidizing agent which attacks the oxide film, said persulfate reacting with the oxide

2

film and being reduced to sulfate. In U.S. Pat. No. 3,275,562 ferric ion, fluoride ion and hydrogen ion are employed to desmut aluminum. In the disclosed solution, it is stated that the hydrogen ion is the primary ingredient which causes smut removal to be effected, while the ferric ion acts to assist said smut removal and inhibits the hydrogen ion attack on the metal surface.

Conventional deoxidizing and desmutting solutions tend to attack the aluminum surface as well as the aluminum oxide film and smut deposits found thereon, said surface attack sufficient to cause a build-up of undesirable metal ions in the bath, resulting in a shorter life for the treating solution. In addition, as the metal surface is contacted with the deoxidizing and desmutting solution, a residual film made up of metals with which the aluminum is alloyed, is frequently formed on the surface. For example, when the surface of a copper containing aluminum alloy is deoxidized, the surface becomes covered with a black speckled smut composed essentially of the alloyed copper and copper oxide. The presence of said residue decreases the protection afforded the surface by a subsequent finishing operation. Most present day deoxidizing and desmutting baths are dumped, due to the resultant residual deposits and the build-up of undesirable metal ions in the bath, well before the deoxidizing and desmutting properties of the solution have been expended.

I have discovered a unique chromeless deoxidizing process employing a chromium-free deoxidizing solution, wherein more efficient deoxidizing is accomplished and residue formation during deoxidizing as well as the build-up of undesirable metal ions in the bath is mitigated. In addition, the novel deoxidizing process of this invention requires little or no replenishment of acid during operation, as the strong acid employed in the deoxidizing solution is not depleted, except for drag-out.

It is an object of this invention, to provide improved deoxidizing compositions and concentrates, improved aqueous deoxidizing solutions, and improved deoxidizing methods for aluminum surfaces.

It is a more particular object of the invention to provide a chrome-free deoxidizing process for aluminum which does not result in residue deposits on the surface and prevents a build-up of undesirable metal ions in the treating bath, thereby increasing the useful life of the deoxidizing solution.

It is also an object of this invention to provide a non-chromate deoxidizing process for aluminum, thereby eliminating toxicity and waste disposal problems.

A concomitant object of this invention is to provide a chrome-free deoxidizing process wherein a controlled etch of the surface is realized and wherein there is little hydrogen ion depletion as the process continues with no acid replenishment necessary as the deoxidizing bath is worked.

Still another object of the invention is to provide a deoxidizing process which allows the aluminum surface to possess uniform low electrical surface resistance without excessive pitting, so that finishing operations such as spot-welding or conversion coating can be effected satisfactorily.

The deoxidizing process of this invention employs chromium-free aqueous acidic deoxidizing solutions for removing the surface corrosion and oxide film and for eliminating any smut deposits which have been formed on the aluminum surface during a prior cleaning or etching step. The deoxidizing solution, during operation of the process, consists essentially of ferric ion, thiourea, and fluoride. Dry compositions or aqueous concentrates can be utilized to prepare and replenish the deoxidizing solution, allowing for continuous operation of the process. The surface of aluminum or its alloy is brought into



## 3

contact with the deoxidizing solution consisting essentially of ferric ion in concentrations from about 5 gram-ions/liter to about 21 gram-ions/liter, thiourea in an amount from about .05 gram/liter to about 3.0 grams/liter and fluoride ion in an amount from about .5 gram-ions/liter to about 2.0 gram-ions/liter. The pH of the deoxidizing solution should be from about .1 to about 1.8, and a strong mineral acid, such as sulfuric acid, can be added to the solution in amounts sufficient to adjust the pH accordingly.

It should be understood that "deoxidizing solution" or "deoxidizing bath" means the aqueous acidic solution employed in the process of this invention. The term, "deoxidizing composition" or "deoxidizing concentrate" means the combination of ingredients in dry or liquid form, respectively, employed to prepare and replenish the deoxidizing solution. The term "aluminum" employed herein encompasses pure aluminum, commercial grade aluminum containing small amounts of impurities, as well as alloys thereof.

An important feature of the process of the present invention is that more effective deoxidizing is accomplished with a slightly increased and controlled surface etch thereby removing the oxide film and smut, while virtually no residues remain on the surface after deoxidizing has been effected. Due to the unique interaction of the constituents of the deoxidizing solution, more effective deoxidizing is realized with no resulting drawbacks such as remaining residues and shortened bath life.

A controlled and increased etch is noticeable with the use of the deoxidizing solutions of the present invention without dependence on hydrogen ion attack of the aluminum surface. The strong acid, such as sulfuric acid, which is employed in the deoxidizing solution in order to adjust the pH of the solution within the range specified herein, is not depleted except for drag-out, and little or no acid replenishment during operation of the process is necessary.

The interactions of the constituents in the present deoxidizing solution are complex and the statements concerning the interactions and purpose of each constituent are postulated from observations and analysis made during operation of the process.

The fluoride ion in the solution tends to increase the etch rate while ferric ion significantly decreases the etch rate to a degree approximately equal to the positive effect of fluoride ion. So, when ferric ion is present in the solution along with fluoride ion, the interaction between these constituents decreases etch rate as compared to a bath wherein fluoride ion is present and ferric ion is absent.

Aside from ferric ion significantly inhibiting the deoxidizing solution from etching the aluminum surface in approximately equal magnitude as fluoride ion positively affects the etch rate on the surface, the ferric ion appears to be an agent which aids in the attack of the oxide film and removal of any smut deposits through an oxidation-reduction mechanism. This property of the ferric ion has been well known in the art.

The interaction of thiourea with the ferric ion in the deoxidizing solution contributes to an increase in surface etch. The presence of thiourea in the deoxidizing solution is important due to its interaction with ferric ion, said interaction decreasing the inhibiting power of ferric ion on the surface etch. In this way, controlled amounts and additions of thiourea to the bath allow for fluoride ion to effect a slightly increased etch. The amounts of thiourea in the deoxidizing solution are critical since the excess of thiourea may not interact with the ferric ion and could effect a decrease in etch rate.

An important aspect of the invention is that even with an increase in surface attack resulting in additional metal ions entering the deoxidizing bath, the presence of thiourea prevents the deposition of metals, with which the aluminum is alloyed on the surface. The thiourea acts as a complexing agent, thereby preventing the metal ions from depositing out onto the metal surface. For example,

## 4

a metal such as copper with which the aluminum is alloyed, is released into the deoxidizing solution when surface attack occurs during operation of the process. As the copper content in the solution reaches a high enough level, metallic copper tends to deposit on the aluminum surface. The thiourea will sequester sufficient copper ions in solution so as to prevent copper deposition on the surface, thereby reducing interference with the deoxidizing process. The thiourea, in sequestering undesirable metal ions, increases the vat life of the deoxidizing solution.

Controlled amounts of thiourea in the deoxidizing bath improve deoxidizing by slightly increasing surface etch due to its interaction with the ferric ion and fluoride ion in solution, and also help retard the problems caused by increased etch by complexing the undesirable metal ions. The controlled increased etch and improved deoxidizing due to constituent interaction is obtained without excessive pitting and non-uniformity of surface appearance.

Thiourea should be present in an amount sufficient to sequester significant amounts of the alloyed metal ions which enter the solution during use and in an amount sufficient to interact with the ferric ion in the deoxidizing solution. Thiourea should be present in an amount from about .05 gram/liter to about 3 grams/liter. It is preferred that there be at least .1 gram/liter of thiourea but no more than 2.0 grams/liter of thiourea in the deoxidizing solution. Should the amount of thiourea in the solution exceed 3.0 grams/liter, there is excess thiourea present over and above that which is necessary to both complex undesirable metal ions and to interact with ferric ion and fluoride ion, and bath control problems occur.

Due to the constant release of metal ions into the bath and such factors as drag-out, thiourea is expended and it is necessary to replenish the deoxidizing solution with thiourea in the replenishing composition or concentrate. In a particular deoxidizing solution during operation, the thiourea can be consumed as it sequesters undesirable metal ions at a rate different than the rate at which other constituents of the solution are being consumed due to drag-out. On some occasions it may be necessary for the thiourea to be added separately to the solution as a replenishing material, in addition to its inclusion as a constituent in the replenishing composition. Should the rate of consumption of the thiourea be about the same as the rate of consumption of the other materials in the deoxidizing solution, it can be added as part of the replenishing composition or concentrate with no separate additions necessary.

One aspect of the invention provides for deoxidizing compositions or deoxidizing concentrates for addition to water or an aqueous acidulated solution to make a deoxidizing solution of the type described herein. An example of a dry make-up deoxidizing composition suitable in the practice of the present invention consists essentially of a ferrous salt, a peroxy sulfate salt, a fluoride salt, and thiourea. It should be noted that when the ferrous salt is placed in an aqueous acidic solution along with an oxidizing agent, such as a peroxy sulfate salt, the ferrous ion in the solution is converted to ferric ion. Thus, at the time of make-up of the aqueous acidic deoxidizing solution, ferric salt can be regarded as equivalent to ferrous salt, and can safely be added should a pure source for ferric salt be available in place of the ferrous salt. For this reason, there is used herein the term "ferric ion" when referring to the presence in the deoxidizing solution of materials added thereto in the form of ferrous salt as well as ferric salt.

Should a dry make-up deoxidizing composition be employed and a ferrous salt be utilized, the ferrous salt and oxidizing agent should not be mixed in one dry composition, since under those circumstances I have found that decomposition can occur to the oxidant. In this case, the oxidizing agent should be added to the solution separately from the ferrous salt. When the deoxidizing solution is initially prepared, the ferrous ion in the aqueous solu-



## 5

tion is oxidized to ferric ion by the suitable oxidizing agent present. Stoichiometric amounts of ferrous salt and oxidizing agent should be added initially to the aqueous acidulated solution so that essentially all the ferrous ion is oxidized. Two dry compositions for make-up of the deoxidizing solution can be utilized, wherein one contains the ferrous salt, either alone or together with other constituents, and the other contains the oxidizing agent, either alone or with other constituents. When a dry make-up composition utilizing a ferrous salt is employed, best results are obtained with one dry admixture consisting essentially of the ferrous salt and thiourea, and a second dry admixture consisting essentially of oxidizing agent and fluoride salt. Formulas 1 and 2 are typical examples of make-up compositions which can be employed concurrently to prepare the aqueous acidic deoxidizing solution.

## FORMULA 1

	Percent by weight
Ferrous sulfate	99.51
Thiourea	.2
Wyandotte Pluronic F127 (nonionic wetting agent)	.29

## FORMULA 2

	Percent by weight
Sodium peroxydisulfate	93.60
Sodium fluoride	6.40

Surface activators, wetting agents, and detergents are desirably included in the deoxidizing composition or concentrate. Such materials enhance the cleaning performance and surface contact of the solution but are not of the essence of the invention since they are used to perform functions substantially similar to the function they perform in prior art solutions. These contact and cleaning agents can be present in the deoxidizing solution in an amount from about .01% to about .1% by weight.

Alternatively, when a ferric salt is employed, the deoxidizing solution can be prepared by employing one deoxidizing composition or concentrate. Formula 3 is a typical example of a deoxidizing concentrate which can be added to an aqueous acidulated solution to prepare the deoxidizing bath.

## FORMULA 3

	Percent by weight
Ferric sulfate	34.11
Hydrofluoric acid (70% solution)	.51
Thiourea	.41
Wetting agent (Wyandotte RA43)	.20
Water	64.77

Formula 4 is an example of a dry make-up deoxidizing composition employing a ferric salt as the source for ferric ion in the deoxidizing solution. This composition can be added to an acidulated aqueous solution to prepare the deoxidizing bath.

## FORMULA 4

	Percent by weight
Ferric sulfate	94.80
Sodium fluoride	4.60
Thiourea	.25
Surfactant	.35

During continuous operation of the process, there is both ferric and ferrous ion in the bath, and ferric ion is continuously being converted to ferrous ion. In order to allow the deoxidizing process to continue, regeneration of ferric ion is necessary so that the ferric ion can perform its function of interacting with thiourea and fluoride to control surface etch, and to allow attack of the oxide film and removal of smut deposits to continue. Any conventional oxidizing agent, such as peroxydisulfate, peroxide, or permanganate, can be added in the replenishing composition in order to oxidize the ferrous ion and regenerate ferric ion. The amount of oxidizing agent which is necessary to be added in the replenishing step will depend on the rate at which the ferric ion is reduced in the deoxidizing

## 6

ing solution. When the ferric ion concentration is depleted to below about 6.0 grams/liter in the working bath it becomes necessary to replenish the deoxidizing solution with a replenishing composition wherein the oxidizing agent is included.

The amount of oxidizing agent which must be periodically added to replenish the deoxidizing solution can be determined from well known titration methods. For example, the ferrous ion content can be determined directly by titration with a potassium permanganate solution. The amount of oxidizing agent added should be stoichiometrically equal to that amount of ferrous ion present. Alternatively, the ferric ion content can be determined, and that amount can be subtracted from total iron content in the bath to establish the ferrous ion concentration. Simple titration methods known to the art, such as the iodometric titration method, can be employed in order to determine ferric ion concentration.

Formula 5 is an example of a dry replenishing composition and Formula 6 is an example of an aqueous replenishing concentrate which can be employed when necessary during operation of the process. It can be observed that Formula 6 does not contain thiourea due to its instability in such a concentrate. Should such an aqueous replenishing concentrate be employed, the thiourea replenishment should be effected separately.

## FORMULA 5

	Percent by weight
Sodium persulfate	88.84
Sodium fluoride	10.52
Thiourea	.64

## FORMULA 6

	Percent by weight
Hydrogen peroxide	8.75
Hydrofluoric acid (70% solution)	3.04
Water	88.21

The replenishing formulations include a source of fluoride ion. As deoxidizing continues, the controlled surface etch will cause small amounts of aluminum to enter the bath as aluminum ion. As aluminum builds up in the solution, fluoride ion is depleted, as soluble aluminum fluoride is formed. It has been found that in order to maintain the solution in continuous operative condition, it is important to regulate the content of fluoride in the solution relative to the aluminum therein so that the concentration of fluoride ion is maintained at the desired level. Unless the fluoride concentration is raised as the aluminum content increases in the deoxidizing bath, the amount of fluoride ion in the bath will be insufficient and the deoxidizing ability of the solution will be retarded.

It has been found that as ferric ion is reduced to ferrous ion during operation of the process, aluminum enters the bath as aluminum ion at a molar ratio of about 1 mole of aluminum for each 3 moles of ferrous ion produced. This aluminum ion forms the soluble aluminum fluoride complex with the fluoride ion present in the deoxidizing bath. Since the ferrous ion concentration is an indication of the amount of aluminum which has complexed with the fluoride ion in the bath, the amount of fluoride necessary to be added to the bath in the replenishing composition can be ascertained from the amount of ferrous ion determined to be in the deoxidizing solution.

A small amount of ferric ion in the deoxidizing solution is lost through drag-out during operation of the process and should be replaced with the appropriate amount of ferric salt or ferrous salt.

During continuing operation of the present process, there is little hydrogen gas evolution evident from the deoxidizing solution and this indicates that little hydrogen ion reduction occurs. The strong mineral acid present at make-up of the deoxidizing solution is not expended during operation and it is unnecessary to replenish with acid during the working of the bath. Should the acid content of the deoxidizing solution become depleted due to drag-



out, small additions of acid may be necessary to adjust the solution pH to the desired level. The pH of the deoxidizing solution should be maintained between about .1 and about 1.8.

In the preferred embodiment of the invention, the deoxidizing composition or concentrate is added to an aqueous acidulated solution consisting of water and a strong mineral acid, such as sulfuric acid. The amount of acid present should be sufficient to adjust the pH of the resultant deoxidizing solution within the range specified hereinabove.

In some instances, the deoxidizing solution can be prepared by adding the deoxidizing composition or concentrate to water with no acid present. The resultant deoxidizing solution will naturally assume a pH less than 1.8, thereby allowing the deoxidizing process to be initiated and continue in the absence of strong acid. Formulas 7 and 8 are examples of compositions which can be employed to prepare a deoxidizing solution by their addition to water with no strong mineral acid present.

#### FORMULA 7

	Percent by weight
Ferrous sulfate heptahydrate	99.51
Thiourea	.2
Wetting agent	.29

#### FORMULA 8

	Percent by weight
Sodium peroxydisulfate	91.12
Sodium fluoride	8.88

Prior to the utilization of the deoxidizing process, the aluminum surface should be cleaned to remove oils, grease, and dirt. The cleaning step can be comprised of any of the conventional cleaning operations known to the art. A vapor degreasing process employing an organic solvent such as trichloroethylene, supplemented and followed by a mild alkaline cleaner, can be employed as a satisfactory method for preparing the aluminum surface. The mild alkaline cleaner will preferably be inhibited to prevent excessive pitting of the aluminum or alloyed surfaces. The metal surface should be rinsed after the cleaning step is completed and thereafter the surface is ready to be treated with the deoxidizing solution.

An alternative cleaning step for castings of aluminum alloys can be effected, wherein an alkaline cleaner is employed to remove oils and mold lubricants, followed by an alkali etch bath. After appropriate rinsing has been completed, the casting is ready to be treated as provided herein.

The aluminum surface, after appropriate cleaning, is prepared for the action of the deoxidizing solution, said solution comprised of from about .05% to about .20% by weight of fluoride ion, from about .5% to about 2.1% by weight of ferric ion, and from about .005% to about .3% by weight of thiourea. The percentages given refer to percent by weight based on the total weight of the solution including the water.

In order for the deoxidizing process to continue effectively and for the most advantages interaction of constituents to occur, the relative amounts of each constituent in the deoxidizing solution must be regulated within desired weight ratios. For each part by weight of ferric ion, in the deoxidizing solution, there should be from about .05 to about .25 part by weight of fluoride ion and from about .01 to about .25 part by weight of thiourea present therein. After the deoxidizing solution is prepared with the relative amounts of constituents present as hereinabove provided, these ratios should be maintained throughout operation of the deoxidizing process by controlling the relative amounts of constituents in the replenishing composition or concentrate.

Fluoride ion can be introduced into the deoxidizing solution in the form of hydrofluoric acid or any soluble salt thereof. The alkali metal fluorides are preferred, particularly sodium fluoride. Ferric ion can be introduced into

the deoxidizing solution in the form of any conveniently available soluble ferrous or ferric salt. Preferably, ferric sulfate or ferrous sulfate should be employed in the deoxidizing composition or concentrate. Should a ferrous salt be employed, then a suitable oxidizing agent should also be added to the deoxidizing solution, said oxidizing agent selected from the group of agents which will oxidize ferrous ion to ferric ion. Examples of such oxidizing agents are persulfate, hydrogen peroxide, and permanganate. In the preferred embodiment of this invention, peroxydisulfate or hydrogen peroxide should be employed. The peroxydisulfate can be added to the deoxidizing solution in the form of an alkali persulfate salt selected from the group consisting of ammonium persulfate, sodium persulfate, and potassium persulfate.

During the deoxidizing process the aluminum or alloyed substrate is brought into contact with the deoxidizing solution under suitable conditions of pH, temperature, and contact time. The deoxidizing solution is preferably applied by conventional immersion or spray techniques.

In order to effectively remove the oxide smut on the surface, contact time between surface and solution should be from about 30 seconds to about 15 minutes. The particular contact time depends upon the type of alloy and the amount of smut, oxide, and surface corrosion to be removed. The deoxidizing process can be operated at a temperature between about 60° F. and about 150° F. The process is preferably operated at ambient temperature, that is between 60° F. and 90° F.

The aluminum surface, after the deoxidizing process has been effected thereon, should be rinsed thoroughly in water assuring that all the deoxidizing solution has been removed therefrom. The metal surface can then be dried in an oven or with hot air and is prepared for any subsequent finishing treatment. The surface can be treated to deposit a protective or decorative coating such as a chromate conversion coating or an anodized coating. The coating produced will possess excellent adherent qualities and will be conducive as a base for a subsequently applied siccative finish.

The following examples are illustrative of this invention and are not considered as limiting for other materials and operating conditions falling within the scope of this invention that might be substituted.

#### EXAMPLE 1

A dry deoxidizing composition was prepared by mixing 102.5 grams of ferrous sulfate heptahydrate, .2 gram of thiourea, and .3 gram of a wetting agent (Wyandotte Pluronic F127), and grinding the admixture until finely particulate. A second dry composition was prepared by mixing 37.2 grams of sodium peroxydisulfate and 3.6 grams of sodium fluoride and grinding said admixture until finely particulate. The two dry compositions were added to 1 liter of an aqueous acidulated solution consisting of 5% B.V. sulfuric acid (66° Bé.), to form the deoxidizing solution.

#### EXAMPLE 2

A deoxidizing composition was prepared by mixing 74 grams of ferric sulfate, .2 gram of thiourea, .3 gram of wetting agent (Wyandotte Pluronic F127), and 3.6 grams of sodium fluoride. The deoxidizing composition was added to 1 liter of an aqueous acidulated solution consisting of 5% B.V. sulfuric acid (66° Bé.) to form the deoxidizing solution.

#### EXAMPLE 3

A deoxidizing concentrate was prepared by adding 682 ml. of a commercially available aqueous ferric sulfate solution containing 50% by weight ferric sulfate, 6.8 ml. of a 70% hydrofluoric acid solution, 6.8 grams of thiourea, and 3.5 grams of Pluronic F127, to 1 liter of water. 125 ml. of the deoxidizing concentrate was added to each 1 liter of an aqueous acidulated solution consisting of 5%



B.V. sulfuric acid (66° Bé.) to form a deoxidizing solution ready for use.

EXAMPLE 4

A deoxidizing composition was prepared consisting essentially of 96.5% by weight of ferrous sulfate heptahydrate, 3.38% by weight of sodium fluoride, and .12% by weight of thiourea. The deoxidizing solution was prepared by adding 8.9 lbs. of the deoxidizing composition to 100 gallons of an aqueous acidulated solution containing 5% B.V. sulfuric acid (66° Bé.), followed by the addition of 3.1 lbs. of sodium persulfate.

3" x 10" panels of 2024T3 alloy were employed in this procedure. The panels were degreased with methyl alcohol and then subjected to a mild alkaline cleaner for 10 minutes at 175° F. The panels were removed from the cleaning bath and rinsed with water.

The panels were then immersed for 15 minutes in the deoxidizing solution prepared as hereinbefore provided, at a temperature of 80° F. They were withdrawn from the deoxidizing bath and there were no visible smut deposits evident on their surfaces. Subsequent to treatment with the deoxidizing solution, the metal surfaces were rinsed with water to remove any remaining deoxidizing solution. The panels were then given a protective conversion coating of the chromate type.

EXAMPLE 5

An aqueous deoxidizing solution was prepared employing Formulas 7 and 8, with 103 grams of Formula 7 and 42 grams of Formula 8 added to each 1 liter of water.

The pH of the resultant deoxidizing solution was measured at 1.72. It should be noted that no mineral acid was utilized in this procedure, and during operation of the process no additions of acid were made.

3" x 10" panels of 2024T3 alloy were employed in this procedure. The panels were degreased in an organic solvent and were then cleaned in a mildly alkaline cleaning solution for 10 minutes at 175° F. The panels were rinsed with water and then immersed in the deoxidizing solution for 15 minutes at 80° F.

After the deoxidizing step had ben completed, the aluminum surfaces showed satisfactory surface etch without pitting and were free of smut.

EXAMPLE 6

The following tests were performed to illustrate the interaction of the constituents in a deoxidizing bath of the present invention. 2" x 3" panels of 2024T3 aluminum alloy were employed in this procedure. The panels were cleaned in an alkaline cleaning bath for 10 minutes at 150° F., said aqueous cleaning bath consisting of sodium metasilicate, tetrasodium pyrophosphate, sodium carbonate, and wetting agents. The panels were then rinsed in tap water and dried. After the panels were processed as hereinbefore described, they were weighed before treatment in the deoxidizing solution.

In order to illustrate the interaction of the constituents in the treating solutions of the present invention, etch rate determinations were made for each of three panels treated with solutions having constituent concentrations as listed in Table 1. After treatment was completed, the panels were rinsed, dried, and reweighed. The etch rates of each of the three panels were calculated and an average was taken as portrayed in Table 1.

The treatment step was accomplished at a temperature of 78° F. and each panel was immersed in the particular solution for a period of 10 minutes. The etch rates listed in Table 1 are expressed in mils per surfaces area per hour.

Bath Nos. 1, 2, 5, and 6 were prepared by adding dry compositions to aqueous acidulated solutions containing 2.5% sulfuric acid (66° Bé.) wherein the concentrations of ferric ion, fluoride ion, and thiourea in the resulting solutions are indicated in Table 1. Bath Nos. 3, 4, 7, and 8 were prepared by adding dry compositions to aqueous acidulated solutions containing 7.5% sulfuric acid (66°

Bé.) wherein the concentrations of ferric ion, fluoride ion and thiourea in the resulting solutions are indicated in Table 1.

It can be observed that thiourea was absent from the compositions employed to prepare bath Nos. 1, 3, 5, and 7. In baths 2, 4, 6, and 8 thiourea was included in the dry deoxidizing compositions so that when these compositions were added to an acidulated aqueous solution, the concentration of thiorea in said baths was .4 gram/liter.

TABLE 1

Bath No.	Constituents	Concentration, grams/liter	Etch rate in mils/surface area/hour ×10 <sup>-2</sup>	Average etch rate
15	Fe+++-----	7.0	11.75, 11.32, 11.71	11.59
	F-----	.82		
	Thiourea-----	.4		
2	Fe+++-----	7.0	11.84, 12.28, 12.24	12.12
	F-----	.82		
	Thiourea-----	.4		
3	Fe+++-----	27.0	17.88, 17.83, 18.58	18.10
	F-----	2.46		
	Thiourea-----	.4		
20	Fe+++-----	27.0	23.09, 21.79, 22.48	22.45
	F-----	2.46		
	Thiourea-----	.4		
5	Fe+++-----	27.0	6.60, 6.38, 6.47	6.47
	F-----	.82		
	Thiourea-----	.4		
25	Fe+++-----	27.0	7.24, 6.79, 7.11	7.00
	F-----	.82		
	Thiourea-----	.4		
7	Fe+++-----	27.0	9.12, 9.28, 9.21	9.20
	F-----	.82		
	Thiourea-----	.4		
8	Fe+++-----	27.0	10.17, 10.15, 10.24	10.19
	F-----	.82		
	Thiourea-----	.4		

The results in Table 1 illustrate that the addition of thiourea to the bath, thereby allowing interaction of ferric ion, fluoride ion, and thiourea to occur, will result in a slightly increased etch rate and a more effective deoxidizing step. Subsequent to treatment with deoxidizing baths 2, 4, 6, and 8 listed in Table 1, the panels were inspected and showed bright, smut-free surfaces.

What is claimed is:

1. A method for removing oxide film and smut deposits from an aluminum surface to prepare said surface for subsequent finishing operations comprising:

(a) cleaning of said surface:

(b) contacting the cleaned surface with an aqueous acidic solution consisting essentially of from about 5 gram-ions/liter to about 21 gram-ions/liter of ferric ion, from about .5 gram-ions/liter to about 2.0 gram-ions/liter of fluoride ion, and from about .05 gram/liter to about 3.0 grams/liter of thiourea, said solution having a pH between about .1 and about 1.8; and

(c) rinsing the surface with water.

2. The method of claim 1, wherein the aluminum surface is contacted with the aqueous acidic solution wherein ferric ion, fluoride ion, and thiourea are present in amounts such that for each part by weight of ferric ion in said solution there is from about .01 to about .25 part by weight of thiourea and from about .05 to about .25 part by weight of fluoride ion.

3. A method for deoxidizing and desmutting an aluminum surface comprising contacting said surface with an aqueous acidic solution having a pH in the range of about .1 to about 1.8, and a temperature of from about 60° F. to about 150° F., and consisting essentially of from about .5% to about 2.1% by weight of ferric ion, from about .05% to about .2% by weight of fluoride ion, and from about .005% to about .3% by weight of thiourea.

4. The method according to claim 3, wherein for each part by weight of ferric ion in the aqueous acidic solution there is from about .01 to about .25 part by weight of thiourea, and from about .05 to about .25 part by weight of fluoride ion.

5. A composition for use in preparing a deoxidizing solution, consisting essentially of a ferric salt, a fluoride salt, and thiourea present in an amount sufficient, upon mixing the composition with an aqueous acidulated so-



11

lution comprising a strong mineral acid and water, to produce a deoxidizing solution having for each part by weight of ferric ion therein from about .05 to about .25 part by weight of fluoride ion and about .01 to about .25 part by weight of thiourea.

6. An aqueous concentrate for use in preparing a de-oxidizing solution, consisting essentially of water, thio-urea, ferric ion, and fluoride ion, wherein for each part by weight of ferric ion in said concentrate there is from about .05 to about .25 part by weight of fluoride ion and about .01 to about .25 part by weight of thiourea.

7. An aqueous solution consisting essentially of from about .5 to about 2.1% by weight ferric ion, from about .05 to about .2% by weight fluoride ion, and from about .005% to about .3% weight of thiourea, said solution having a pH in the range of about .1 to about 1.8, and

12

for each part by weight of ferric ion in said solution there is from about .05 to about .25 part by weight of fluoride ion and about .01 to about .25 part by weight of thiourea.

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