

UNITED STATES PATENT OFFICE

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COMPOSITION AND METHOD FOR CLEANING
ALUMINUM PREPARATORY TO SPOT
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9 Claims. (Cl. 252—136)

1

This invention has to do with the finishing of aluminum surfaces.

To prepare aluminum surfaces and the surfaces of aluminum alloys for welding or painting, and particularly for spot welding, it is desirable first to finish the surface by removing the oxide and otherwise thoroughly cleaning it, which operation will be hereinafter characterized as deoxidizing.

This invention is directed more particularly to an aluminum cleaning bath which may be used cold—that is, at or around ordinary room temperatures ranging typically from about 65° F. to 85° F.

The aluminum deoxidizing baths of the prior art have been of both the "cold" and "hot" type, but all have been subject to rather serious shortcomings.

The cold baths of the prior art have been necessarily highly corrosive to be operable, depending for their effectiveness upon a relatively rapid attack upon the surface being treated—a typical immersion period being of the order of 30 seconds. Moreover, they are somewhat selective in their attack, with the result that they completely dissolve only certain surface constituents and leave the undissolved and galvano-deposited constituents on the surface of the work in the form of a smut which requires a subsequent removal operation.

The heated baths—that is, baths which, for activating purposes, are necessarily heated to temperatures ranging from 120° F. to 212° F.—have been subject to substantially the same objections, plus the impossibility of maintaining uniform temperatures under practical working conditions, which latter is a major objection since those prior art baths require a rather critical time-temperature relationship. For instance, articles having relatively heavy or thick sections are slower in coming up to the temperature of the bath than are articles having lighter sections, with the result that the two are attacked by the bath at different speeds. And when heavily loaded baskets of work are immersed in the bath, they chill the bath long enough to upset the delicate time-temperature relationship of the method employed.

Some of the practical difficulties experienced with prior art practices may be better understood

2

when we consider the fact that not infrequently, due to the rapidity of the attack of those baths, it is found difficult to get a large sheet into and out of the bath rapidly enough to prevent over-treatment.

I attribute those shortcomings to the uncontrolled, highly corrosive solutions heretofore employed; to the failure to take into account the activating or catalyzing agents present as impurities in the chemicals and tap waters used; to the use of heat as the accelerating agent and to the difficulties of maintaining any dependable control of the pH value and the activation of such baths.

It is among the chief aims of my invention to provide an aluminum deoxidizing bath which is fully controlled in its attack upon the surface being treated, and in which over- or under-treating may be avoided.

It is a further object to provide an effective and economical maintenance of such a bath at a uniform pH value to compensate for the usual depletion of the acidity caused by the neutralizing effect of the metal which it dissolves.

It is also an object to provide a bath which will operate at ordinary room temperatures, without the necessity of heating or cooling means.

Another object is to reduce the number of steps required in the processing cycle by eliminating the final bright dip or wiping operation as well as a corresponding number of rinses.

Another object is to minimize the deposition on the work of corrosion promoting elements which tend later to cause failure of the work by atmospheric or electrolytic corrosion.

It is another object of my invention to provide a bath of this character which may be used in inexpensive equipment.

Another object is the provision of an aluminum cleaning bath in which there is an absence of hazardous fumes and which therefore requires no ventilating equipment.

Still further advantages are inherent in my invention and how those as well as the foregoing specified objects are attained will be best understood from the following detailed explanation of a preferred adaptation thereof.

In general, I utilize a cold bath which is relatively slow in its attack upon the surface being treated, which provides a very low pH value, and

3

which may be economically maintained at its original low pH value. Preferably I employ a solution having a phosphoric acid base augmented by the addition of a highly dissociated, non-halogen oxygen mineral acid in sufficient quantity to bring the pH value of the bath down to the desired low figure, the bath being maintained at the desired value by subsequently adding, from time to time, additional quantities of the latter acid. Moreover, I utilize a chemical agent as the catalyzer or activator, after first taking into account the activating radicals present as impurities in the acids and water of the bath, so that at all times I am able to maintain accurate control and uniformity of operation.

I am aware that phosphoric acid has been used as an oxide removing agent for aluminum, but heretofore it has been deemed necessary to use it in relatively strong concentrations, of the order of 10% by weight or more, in order to obtain a bath of operable acidity. It has also been deemed necessary, in prior uses of phosphoric acid baths, to maintain the bath at relatively high temperatures ranging from 120° F. to 212° F. in order to activate the bath in its attack upon the work. No allowance has been made in those prior art practices for the activating radicals present as impurities in commercial grade acids and in tap waters, and this failure, added to the difficulties of maintaining a uniform bath temperature, have resulted in frequent injurious over-treatment of the surfaces, particularly in the case of relatively thin sheets.

The previous necessity for using relatively strong solutions of phosphoric acid I attribute to the tri-basic nature of the chemical. That is, ortho-phosphoric acid comprises three available acid hydrogen ions of widely variant acidity. Only one of those ions is really strongly acidic. Consequently, it has been found that only very strong solutions of the phosphoric acid will provide the high acidity or hydrogen ion concentration necessary to dissolve aluminum oxide and to prevent the formation of undesirable deposits of aluminum phosphate on the surface.

In the preferred adaptation of my invention, I use, as the base of my etching solution, a relatively weak concentration of ortho-, pyro-, meta-, or poly-phosphoric acid, the optimum being of the order of about 5% by weight. I obtain the desired acidity of the bath by augmenting it with a relatively inexpensive, highly dissociated, non-halogen oxygen mineral acid, preferably sulphuric acid, although nitric or chromic acid will suffice. I add such additional minute quantities of this dissociated acid, as the acidity of the bath becomes depleted, as may be necessary to maintain the initial pH value.

I prefer initially to prepare and to maintain the bath at a pH value of below 1.0, the optimum being about 0.5, although I do not limit my intention to such figures since I find my bath to function at pH values ranging from below zero upwardly to about three. To bring my bath to a 0.5 pH value the quantity of the augmenting acid required depends upon the alkalinity of the tap water used. To a typical water carrying a total alkalinity of 300 parts per million expressed as CaCO_3 , I add 4% by weight of concentrated sulphuric acid (specific gravity 1.84).

I have said that one of the outstanding shortcomings of prior art practices has been the absence of any uniform activation of the attack of the bath upon the aluminum being treated. In all tap waters and commercial grade chemicals

4

there are present, as impurities, radicals which act as catalyzing agents. No account has heretofore been taken of those radicals, with the result that as the solutions have been heated to activate etching activity, they have been somewhat erratic in their attack, resulting in over-treatment and injury to the work. Furthermore, apart from the presence of such impurities, as hereinbefore stated, reliance upon activation by heat has been unsatisfactory for the reason that, under practical working conditions, it is difficult to maintain a uniform temperature of the bath and it also requires relatively expensive equipment and produces hazardous fumes.

I find that the impurities most responsible for this activating effect are the halide radicals, particularly the chlorides and fluorides, and in my bath I positively and accurately control the action by first determining the amount of active radicals present in the bath. If there is an excess over and above enough to cause the activation desired to provide a given immersion period, I modify or neutralize them to the necessary extent by adding well-known neutralizing chemicals such, for instance, as silver nitrate for the chlorides and iodides, or calcium nitrate for the fluorides, or if there is an insufficient amount of them in the bath I add a suitable activating agent in an amount sufficient to provide the desired etching rate. Preferably, I add sodium fluoride, NaF , because it is an efficient catalyst, it is non-hygroscopic, non-corrosive and may be safely handled with the bare hand. Furthermore, it is in finely divided powder form suitable for measuring in minute quantities. Other halides are usable, however, among them being chlorides, iodides, bromides, bifluoride of sodium and the fluorides and bifluorides of other metals such as potassium, aluminum, lithium and magnesium. Also the silicofluorides, fluoborates and aluminofluorides may be used since they dissociate to some extent into free hydrofluoric acid under the strong acid conditions of the bath.

The total concentration of the catalytic agent which I find preferable under normal conditions is from .01% to 2.0% by weight; the principal determining considerations being the immersion time assigned to the operation. The desired immersion period is generally of the order of four minutes, although it may vary from 30 seconds to 20 minutes in different plants. For a four minute immersion period I prefer to use about 0.2% by weight of catalyst. Also I might mention that the gage of the aluminum sheet being treated may be a contributing factor in determining the optimum catalyst content of the bath as well as the immersion time, because lighter gage sheets, or those whose surfaces have been severely worked mechanically, and heavier gage sheets may respond to the bath differently. During the course of immersing in and removing work from the bath, some of the catalyst is usually taken out of the bath on the work, and my invention contemplates subsequent addition of sufficient catalyst to compensate for such depletion.

In the operation of my bath, the rate of attack on the metal is relatively slow and consequently the quantity of irritating fog in the surrounding atmosphere is materially reduced. There are no hazardous fumes. I am able to eliminate the fog entirely by introducing into the bath a synthetic detergent and foaming agent, commonly known as a wetting agent. Suitable wetting agents are the acid stable sulphonated or sulphated de-

5

derivatives of long chain hydrocarbons, alcohols, fatty acids or substituted aromatic compounds, or they may be phosphonated derivatives of those compounds, or substituted nitrogen compounds having surface active properties, or they may be glucocides which exhibit foaming properties. I prefer to use the sulphonated phenolic ethers, or the alkyl aryl sulphonates. The wetting agent provides a blanket of foam which collects the hydrogen gas bubbles and retains the entrained liquid which would otherwise be carried into the air. The detergent ability of the wetting agent, by lowering the interfacial tension of the bath, serves to separate masking soil films from the aluminum surface, thereby initiating uniform solvent action along the entire bare aluminum surface practically at the instant of submersion in the bath. By lowering the surface tension of the bath, the wetting agent serves to lower the maximum bubble size so that the hydrogen gas bubbles will detach themselves more readily from the aluminum surface being treated and thereby permit efficient penetration of the bath.

The efficiency of my bath has been particularly demonstrated in its application to finishing aluminum surfaces preparatory to spot welding operations. For instance, the prior art aluminum deoxidizing baths are so inefficient that, in the aircraft industry for instance, spot welding is allowed only on secondary structures, and even then production is necessarily slowed for frequent cleaning of electrode tips. Present baths and methods permit only about 100 spot welds between cleanings of the tips. On the other hand, by my bath and process, the surfaces are so effectively finished and smut-free that welding of primary structures is possible and more than 400 spot welds can be made between cleanings of the electrode tips.

While I have named specific chemicals and procedures in course of explaining a presently preferred adaptation of my invention, I wish it understood that, within the broader concept of my invention as defined by the following claims, it contemplates the use of equivalent chemicals, steps and procedures.

I claim:

1. A method for cleaning the surface of aluminum articles which comprises immersing successive aluminum articles in a cold aqueous phosphoric acid bath having a pH below about 3 and an initial concentration of about 0.01% to 2.0% w. of a substance capable of yielding a halide radical, withdrawing the cleaned articles from the bath in about 20 minutes to about 30 seconds varying inversely with the concentration of said substance, and adding sufficient of said substance to the bath from time to time so as to maintain its concentration approximately within this range.

2. A method for cleaning the surface of aluminum articles which comprises: immersing successive aluminum articles in a cold aqueous bath, which bath has a pH below about 3 and comprises a phosphoric acid, sulfuric acid and an initial concentration of about 0.01% to about 2.0% w. of a substance capable of yielding a halide radical, withdrawing the cleaned articles from the bath in about 20 minutes to about 30 seconds, said time varying inversely with the concentration of said substance, adding successive increments of an acid to maintain the acidity of the bath, and adding successive increments of said substance to maintain its concentration in the bath.

6

3. A method for cleaning the surface of aluminum articles which comprises: immersing successive aluminum articles in a cold aqueous bath, which bath has a pH below about 1 and comprises a phosphoric acid, sulfuric acid and an initial concentration of about 0.01% to about 2.0% w. of a substance capable of yielding a halide radical, withdrawing the cleaned articles from the bath in about 20 minutes to about 30 seconds, said time varying inversely with the concentration of said substance, adding successive increments of an acid to maintain the acidity of the bath, and adding successive increments of said substance to maintain its concentration in the bath.

4. A method for cleaning the surface of aluminum articles which comprises: immersing successive aluminum articles in a cold aqueous bath, which bath has a pH below about 3 and comprises a phosphoric acid, a highly dissociated non-halogen mineral acid and an initial concentration of about 0.01% to about 2.0% w. of a substance capable of yielding a halide radical, said substance comprising a fluoride, withdrawing the cleaned articles from the bath in about 20 minutes to about 30 seconds, said time varying inversely with the concentration of said substance, adding successive increments of an acid to maintain the acidity of the bath, and adding successive increments of said substance to maintain its concentration in the bath.

5. A method for cleaning the surface of aluminum articles which comprises: immersing successive aluminum articles in a cold aqueous bath, which bath has a pH below about 3 and comprises a phosphoric acid, a highly dissociated non-halogen mineral acid and an initial concentration of about 0.01% to 2.0% w. of a substance capable of yielding a halide radical, said substance comprising a silicofluoride, withdrawing the cleaned articles from the bath in about 20 minutes to about 30 seconds, said time varying inversely with the concentration of said substance, adding successive increments of an acid to maintain the acidity of the bath, and adding successive increments of said substance to maintain its concentration in the bath.

6. A phosphoric acid cleaning bath having a pH between about 0 and about 3 and comprising about 0.01% to about 2.0% w. of a substance which furnishes a halide radical.

7. An aqueous cleaning bath having a pH between about 0 and about 3, said bath comprising: a phosphoric acid, a highly dissociated non-halogen mineral acid and about 0.01% to 2.0% w. of a substance which furnishes a halide radical.

8. An aqueous cleaning bath having a pH between about 0 and about 3, said bath comprising: a phosphoric acid, sulphuric acid and about 0.01% to about 0.2% w. of a substance which furnishes a fluoride radical.

9. A method for cleaning the surface of aluminum articles which comprises: immersing successive aluminum articles in a cold aqueous bath, which bath has a pH below about 3 and comprises a phosphoric acid, a highly dissociated non-halogen mineral acid and an initial concentration of about 0.01% to about 2.0% w. of a substance capable of yielding a halide radical, said substance comprising a fluoroborate, withdrawing the cleaned articles from the bath in about 20 minutes to about 30 seconds, said time varying inversely with the concentration of said substance, adding successive increments of an

7

acid to maintain the acidity of the bath, and adding successive increments of said substance to maintain its concentration in the bath.

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