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COMPOSITION FOR CLEANING ALUMINUM AND ALUMINUM ALLOY SURFACES PREPARATORY TO SPOT WELDING

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This invention relates to a cleaning bath and method for the preparation of aluminum and aluminum alloys prior to spot welding.

In order to obtain more strength in aluminum structural elements, it is customary to employ aluminum alloys containing minor amounts of heavy metals, such as, for example, up to about 5% copper, and smaller amounts of manganese, iron, etc.

However, with conventional cleaning baths and processes, traces of these heavy metals apparently dissolve in the bath and are then deposited on the surface of the aluminum alloy so that a copper smut may be produced on the finished surface. This is disadvantageous both in that it fouls the electrode tips and in that the weld buttons are of unequal strength due to the unpredictable occurrence and variation of such galvano deposits. Consequently, in aircraft construction, for instance, spot welds have been permitted only in secondary structures.

Accordingly, it is an object of the present invention to provide an aluminum cleaning bath which does not allow heavy metals to plate back on the treated surface.

Another purpose is the provision of a highly effective and economical method of deoxidizing aluminum alloys, which may be carried out even at room temperatures without heating the bath, and is of especial utility in preparing such alloys for spot welding.

Additional objects will be apparent from the present specification and claims.

We have discovered that the foregoing objects may be accomplished by use of an aqueous acidic solution containing, dissolved therein, any substance which dissociates in the solution into a pyrophosphate radical and one or more other ions. The other ions, constituting the remainder of the products of the dissociation of the substance, have no appreciable effect in the bath unless they happen to be hydrogen ions, in which case they could affect the acidity of the solution. Such dissociated substance may be either pyrophosphoric acid ($H_4P_2O_7$) or one or more soluble salts thereof. The salts may be either neutral, basic or acid salts, organic or inorganic. Particularly preferred are the alkali and ammonium pyrophosphates.

Suitable metallic salts include $Na_4P_2O_7$, $Na_2H_2P_2O_7$, $K_4P_2O_7$, $K_2H_2P_2O_7$, $Li_4P_2O_7$, $Li_2H_2P_2O_7$, $Ca_2P_2O_7$, $CaH_2P_2O_7$, $Mg_2P_2O_7$, $MgH_2P_2O_7$, and the like. The corresponding pyrophosphates or Sr, Ba, Be, Zn, Cd, Al and Cr with their acid or basic (e. g. $(AlOH)_2P_2O_7$) pyrophosphates are suitable

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to the limits of their solubilities in the acidic solution.

Suitable non-metallic salts include the ammonium and amino pyrophosphates of the formula $(R_4N)_{4-x}M_xP_2O_7$ wherein the several Rs represent the same or different monovalent radicals such as H+, methyl, ethyl, propyl, butyl, pentyl, etc., and their homologues; the several Ms represent a hydrogen ion or the same or diffierent monovalent metallic radical such as K, Na, Li, ½Ca, ½Mg. etc.; and x is 0, 1, 2 or 3.

Such organic (as well as inorganic) pyrophosphates may be prepared by dissolving or dispersing, for example, mono-, di-, tri-, or tetra-equivalent weights of the desired amine or amines in water containing sufficient ice to prevent superheating, and adding with stirring, the required amount of pyrophosphoric acid. For example, the tetra substituted pyrophosphate of triethanolamine may be prepared in solution equivalent to 10% of the tetrasodium pyrophosphate by dissolving 560 grams of commercial triethanolamine (av. equivalent wt., 140) in 1020 grams of water, adding 902 grams of chopped ice, and then adding 178 grams of pyrophosphoric acid in a thin stream with vigorous agitation. By the end of the reaction the last bit of ice will have melted and the batch will have warmed to room temperature, or about 60° F.

The necessary acidity of the cleaning bath may be obtained from ortho phosphoric acid (H_3PO_4), although other non-halogen acids such as sulphuric, nitric, or chromic may be used in whole or part, and employment of a pyrophosphate acid salt may also augment the acidity. A preferred pH for the bath is on the order of 1.2 or less.

Whereas phosphoric acid baths which have been used for aluminum cleaning in the past have required a temperature of about 120° F. and have had to be carefully controlled to avoid overtreatment of the metal, our bath containing pyrophosphate radical preferably should not be heated, but is preferably used at room temperature, and no special precautions need be taken to prevent overtreatment of the aluminum. Peculiarly enough, our solution seems to increase in effectiveness with age and use. In fact, heating of our solution above room temperature, or about 60° F., causes progressive conversion of the pyrophosphate into orthophosphate and thus tends to destroy or impair its effectiveness. Even at 120° the conversion is substantial. It is of interest also that other condensed phos-

phates such as metaphosphate, hexametaphosphate and other polyphosphates do not produce an effect comparable to the pyrophosphate.

The substance yielding the pyrophosphate radical may be present in any proportion, a preferred range being about 0.25% to 20% by weight of the pyrophosphate radical. Phosphoric or other acid may be used in proportions on the order of 5% up to 50% or more by volume, 20% being preferred as an optimum.

A particularly satisfactory action may be obtained by using an aqueous solution of sodium pyrophosphate and orthophosphoric acid in a ratio of 0.01 to 0.5 parts by weight of the pyrophosphate to each part of the acid.

Generally the acid is added to the bath prior to the salt since the solubility of the latter is greater in acidic media.

In order to promote the removal of oleaginous films adhering to the aluminum surface, a surface active agent or dispersant which will lower the interfacial tension between oil and water, may be added to the bath. Suitable agents are listed in "Industrial and Engineering Chemistry," Vol. 35, No. 1, January 6, 1943, pages 126–130. Particularly applicable groups are phosphonates, sulfonates, and nitrogenous compounds such as quaternary ammonium salts, amines, amides, etc., which are soluble and stable in acidic media.

Of the fatty acid or tertiary alkyl amines or amides, oleic amine or amide is particularly applicable. Of the alkyl aryl or fatty acid sulfonates the following are particularly applicable: alkyl phenylene alkali sulfonate, isopropyl or isobutyl napthalene alkali sulfonate, tetrahydronaphthalene alkali sulfonate, monoethyl or monobutyl phenyl phenol alkali or amino monosulfate, monobutyl diphenyl alkali monosulfate, dibutyl phenyl phenol alkali disulfonate, monoethyl phenyl phenol guanidine monosulfonate, petroleum sulfonates, and sulfonated alkylated benzene. Of the alkali fatty acid amine sulfonates, $C_{17}H_{33}CONH—CH_3C_2H_4SO_3Na$ is particularly applicable. Of the quaternary ammonium salts, alkyl dimethyl benzyl or pyridinium ammonium salts is particularly applicable. Also particularly applicable are 12–18 C hydrocarbon substituted amides of alkyl phosphate, phosphorated higher alcohols, aryl alkyl polyether alcohol condensates, aryl alkyl polyether sulfonates and alkali fatty acid amide sulfonates.

Also applicable are coupling agents or mutual solvents for oil and water such as ethylene glycol mono- or di-alkyl ethers, and diethylene glycol mono alkyl ethers, where alkyl is generally methyl, ethyl, butyl, phenyl, etc. Quantities on the order of about 1% to 30% (weight or volume) of either class of substances are indicated, although this is not critical.

A specific example of our cleaning bath is:

75% orthophosphoric acid	ml.	200
Tetrasodium pyrophosphate	grams	50

Water, quantity sufficient to make 1 liter.

Another example, employing an oleaginous loosening agent is:

75% orthophosphoric acid	ml.	200
Tetrasodium pyrophosphate	grams	50
Ethylene glycol monobutyl ether	ml.	20

Water, quantity sufficient to make 1 liter.

In addition, or in lieu of ethylene glycol monobutyl ether, there may be added 5 to 10 g. per liter of lauryl or cetyl dimethyl benzyl ammonium sulfate.

The period of treatment of an aluminum or aluminum alloy article in the bath is not at all critical with our method, the range being from one minute to one hour, although the optimum range is from five to 15 minutes.

This is a continuation-in-part of our copending application of the same title, Serial No. 523,650, filed May 1, 1944, now abandoned.

While our invention has been described from time to time by reference to specific amounts and proportions, it is to be understood that these are given by way of illustration only and these may be varied within the scope of the appended claims.

We claim:

1. The method of cleaning aluminum and and aluminum alloy surfaces to adapt them for spot welding which consists in subjecting said surfaces to the action at a temperature below about 120° F. of an aqueous solution of sodium pyrophosphate and orthophosphoric acid in a ratio of about 0.01 to 0.5 parts by weight of the pyrophosphate to each part of the acid, which acid is present in about 0.25% to 20% by weight.

2. A composition for cleaning aluminum and aluminum alloy surfaces to adapt them for spot welding, which consists of an aqueous acidic solution of about 5% to 50% by volume of a nonhalogen inorganic acid and about 0.25% to 20% by weight of another substance which is dissociated in such solution into a pyrophosphate radical and another ion.

3. A composition for cleaning aluminum and aluminum alloy surfaces to adapt them for spot welding, which consists of an aqueous acidic solution of about 5% to 50% by volume of phosphoric acid and about 0.25% to 20% by weight of a substance which is dissociated in such solution into a pyrophosphate radical and another ion.

4. The composition of claim 2 wherein said other substance comprises a water-soluble pyrophosphate.

5. The composition of claim 2 wherein said other substance comprises an alkali pyrophosphate.

6. The composition of claim 2 wherein said other substance comprises tetrasodium pyrophosphate.

7. A composition for cleaning aluminum and aluminum alloy surfaces to adapt them for spot welding, which consists of an aqueous solution of a sodium pyrophosphate and orthophosphoric acid in a ratio of 0.01 to 0.5 parts by weight of the pyrophosphate to each part of the acid.

8. A composition for cleaning aluminum and aluminum alloy surfaces to adapt them for spot welding which consists of the following ingredients and relative proportions thereof:

75% orthophosphoric acid	ml.	200
Tetrasodium pyrophosphate	gms.	50

Water sufficient to make 1 liter.

9. A composition for cleaning aluminum and aluminum alloy surfaces to adapt them for spot welding which consists of the following ingredients and relative proportions thereof:

75% orthophosphoric acid	ml.	200
Tetrasodium pyrophosphate	gms.	50
Ethylene glycol monobutyl ether	ml.	20

Water sufficient to make 1 liter.

10. A composition for cleaning aluminum and aluminum alloy surfaces to adapt them for spot welding which consists of an aqueous solution of

about 5% to 50% by volume of orthophosphoric acid and about 5% by weight of sodium pyrophosphate.

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