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COATED ALUMINUM

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This invention relates to coated aluminum; and it comprises an article of aluminum or of aluminum alloy wholly or partially covered with an integrally united coating containing Al_2O_3, SO_3 and H_2O in proportions corresponding to a sub-sulfate and produced by making said article an anode in sulfuric acid of a specific gravity between 1.5 and 1.7 with a low voltage current; said coating being of substantial thickness, usually of the order of a thousandth of an inch (0.0001 to 0.0015), being minutely porous or pervious, and taking up dyes with readiness and with substantial uniformity at all points, and evincing no crystallinity under X-ray examination but having a laminæ structure with an extremely hard and extremely thin, glaze-layer next the metal and a much thicker but less hard outer layer integrally united thereto, the hardness of the layer as a whole being great enough to permit buffing and polishing; and it also comprises such an article, dyed or undyed, having the pores filled to give a composite impervious coating; all as more fully hereinafter set forth and as claimed.

As is well known, metallic aluminum is always covered with a film of aluminum oxid formed by the action of air. This film is impervious and is self-renewing in the sense that where it is removed, cracked or broken it is, practically at once, renewed by the action of the air. Being formed at the expense of the metal and being wholly impervious it is of necessity extremely thin, being possibly mono-molecular. Naturally, where it forms further attack on the underlying metal is precluded. While this film is an excellent protection against corrosion and is not unsightly, its existence practically renders impossible the ordinary decorative treatments which can be applied to other metals. It is, for example, difficult to make different finishes by different ways of buffing or polishing; and paints, lacquers and varnishes do not hold well to it; both because its impervious nature prevents anchorage and because most coating materials do not cohere to alumina; do not "wet it", so to speak. For this reason aluminum articles are seldom decorated in any way. Plating aluminum with other and more ornamental metals is quite difficult.

In the prior art, attempts have been made to improve on the natural oxid films; artificial oxid films being formed in various ways, mostly electrolytic. The object being to protect the metal, impermeable coatings are sought and these are necessarily extremely thin. With formation of an impervious coating, attack on the underlying metal ceases. These films are usually quite hard and rigid; and are too thin to be buffed, polished or mechanically finished. They do not afford a good base for decorative finishes. While staining and dyeing have been proposed, neither has been successful.

Aluminum articles under the present invention carry a hard, pervious coating formed under oxidizing conditions at the expense of the underlying metal; this coating being of substantial thickness, say 0.0001 to 0.0015 inch, and being composed of Al_2O_3, SO_3 and H_2O in some form of combination. With aluminum alloys containing silicon, the coating may also contain a little SiO_2. While the coatings are pervious, the pores are not visible, being of sub-microscopic magnitude. The coating has a more or less developed structure, there being a relatively thick hard outer layer and a relatively thin glaze-like still harder underlayer next the metal. The glaze layer is sometimes only 5 per cent or so of the total thickness of the coating. The coating as a whole is mechanically strong and can readily be buffed or polished to a smooth finish. In color the coating is white or light gray, coatings high in silica being sometimes a darker gray. The coating withstands heat well and I sometimes bake it during or prior to finishing. It takes dyes readily.

In finished articles under the present invention, I may simply buff and polish the described coating. In buffing and polishing, the stearic acid or grease of the ordinary buffing compositions suffices to fill the pores and make the coating impervious. However, I sometimes use special impregnants such as lanoline. Usually, but not always, I dye or stain the coating.

In another and copending application, Serial No. 463,351, I have described and claimed a method of producing relatively thick coatings of this type upon aluminum and aluminum alloy articles. In this method, aluminum is made an anode in a somewhat diluted sulfuric acid, the acid usually being around 70 per cent of H_2SO_4. The result is formation of a coating having the described characteristics.

In this method of operation the first result of the passage of current is the production of an extremely thin coating of flinty hardness. This film, however, is pervious and attack proceeds with building up of an overlying layer; the main body of the coating of the present invention. There is at first a surge of current and then the current settles down to a steady value. Within limits, any thickness of coating desired may be produced at the expense of the underlying metal which is correspondingly etched. The coating is porous and the pores extend to the actual metal. The coating is at first transparent but becomes translucent and whitish as it thickens. The coating is, as stated, susceptible of buffing and polishing by the usual tools; being polished with readiness. It withstands bending, stamping and punching to a reasonable extent. Although actually pervious the coating affords a reasonable degree of protection to the underlying metal because of the extreme fineness of the pores which are, as stated, of sub-microscopic dimensions. A little grease or oil of any kind suffices to seal off these pores. Lanolin, petrolatum, beeswax, etc. may be used. It is noted as a matter of interest that when these filling materials are once applied they are withdrawn only with difficulty by the action of gasoline or other solvents; a phenomenon which may be due to some sort of adsorptive action by the aluminum compounds forming the coating. It is also noted that the stearic acid and grease of buffing compositions are similarly taken up.

The coating treatment may be applied to flat aluminum metal subsequently stamped into form for certain types of articles and specific uses or it may be applied to the finished articles. The shape of the article makes no particular difference in coating; deep recesses being coated as readily as flat surfaces. Before coating the article should be finished and thoroughly cleaned.

The coating contains aluminum oxid, SO_3 and water of hydration. The composition of the coating as a whole often empirically corresponds to about $3Al_2O_3.5H_2O.SO_3$; that is to a hydrated subsulfate, or extremely basic sulfate, of aluminum. No evidence of crystalline structure can be found by X-ray examination. The coating as a whole may contain upwards of 16 per cent SO_3 and 18 per cent H_2O. The thickness of the coating can readily be made around 0.001 inch; or about five times the thickness of the usual nickel plating. On careful examination the coating is found to be, so to speak, graduated in hardness from surface to base. Mechanically, the aluminum, the glassy linking layer, and the outside layer behave as if they are integrally united. The described coating may be produced by the method of the acknowledged application, or by other methods.

The coating is colorless or grayish white and can be readily and permanently dyed, taking up and holding those dyes which are customarily used with mordants. In other words, the coating is readily converted into a "lake" of any desired color or hue. Other dyes may be used.

Decorative effects in the coating produced as described can be achieved in a number of other ways. Its thickness is sufficient to permit buffing and polishing to an attractive finish. Buffing, polishing and mechanical finishing of the coated article is done after dyeing. It is found that the coating, both before and after buffing, will take up oils and oily materials. Colored oils give various decorative effects. Paints, stains, varnishes and lacquers applied to the article give a good bond to the coating. Various chemical treatments are possible. The coated article may, for example, be immersed in a fairly concentrated solution of sodium dichromate and allowed to drain and immersed in a solution of lead acetate. Lead chromate, an inorganic pigment, is chemically precipitated within the pores of the coating by the resulting metathetical reaction. By treating with resin soaps, resinates may be produced in the pores. This is advantageous where an additional keying action is desired in lacquering or enameling.

The strength of the sulfuric acid electrolyte used in the anodic treatment is of considerable importance. The best quality of coatings under the present invention are now being obtained in 64 to 65 per cent acid. A range of acid strength between 60 and 77 per cent H_2SO_4, that is, a specific gravity of 1.5 to 1.7 gives excellent coatings of the type here described and claimed. With acid of higher specific gravity than 1.7 the conductivity is so small that it is difficult to secure efficient current densities, while lower concentrations of acid, between 35 and 60 per cent, cause excessive etching and attack on the aluminum with poor coatings as a result. In making coatings with concentrations of sulfuric acid between 60 and 77 per cent, it has been found highly advantageous to add some glycerin to the electrolyte. This aids in preventing local action and makes for uniformity of coating. Presence of glycerin is useful in retarding attack of the acid on the coating and solution of metal. I use ordinarily about one part by volume of glycerin to 15 parts

by volume of 1.5 to 1.7 acid. Various other addition agents, such as cresol and other phenols, may be used. Phenols when used are advantageously first sulfonated.

Other acids, such as nitric acid, are not here the equivalent of sulfuric acid since they cause surface roughening and attack without production of the type and composition of coating here desired.

In operation, the apparatus in which the anodic coating is effected is most conveniently made of stoneware or other ceramic or vitreous material. However, containers of wood or metal, lined with materials resistant to sulfuric acid, such as pitch, rubber or sheet lead, may be used. The cathodes may be of any convenient material, but I find cathodes of ordinary chemical lead best adapted. The size and shape of the cathodes, of course, vary according to the work to be done; but for many purposes they may be located on the side walls of the bath and cover about 50 per cent of the side wall area. With lead lined containers the lead lining may very conveniently serve as a cathode. The articles to be treated may be hung in the bath upon the usual conducting rods. Pointed clamps may be used with sufficient passage of current so that the uncoated area in the finished article is merely an imperceptible spot. The direct current voltage used is ordinarily about 12 volts between terminals. With a voltage of this order no rheostats or regulating devices are necessary. The bath is cooled in any of the ordinary ways. With large baths, cooling coils or cooling jackets are generally desirable. Circulation of the electrolyte, with agitation thereof, in well known ways, is also desirable. Heat is evolved in the operations. It is best to keep the temperature between 20° to 30°, preferably at 25° C. The anode current density, with the usual spacing between anodes and cathodes, is ordinarily between 6 and 10 amperes per square foot of surface of the article being treated.

While I have described making the aluminum an anode in a sulfuric acid bath with employment of direct current of the usual type used in plating, an alternating current may be used in lieu of direct current. The "rectifier" action of aluminum makes this feasible. I have secured good coatings with low voltage alternating current. Even 8 volts have sufficed. In some instances this applicability of alternating current is advantageous since a small step-down transformer can be used with ordinary 60 cycle lighting current in lieu of the more complex equipment necessary in securing low voltage direct current. In using alternating current, aluminum articles to be coated may form both the electrodes in the acid bath.

The aluminum articles to be coated should be subjected to the usual preliminary cleaning treatment. When a lustrous coating is wanted the aluminum should be buffed before cleaning. In any event, grease and other foreign matters should be removed. The aluminum articles can be given a coating of ornamental design by blocking off portions of the surface with asphaltum base stop off or other acid resisting materials and protecting designed portions from the anodic treatment.

For most purposes the time usually required for the anodic treatment to produce the desired coating as above described is 10 to 30 minutes; the time varying with different alloys in producing a given thickness of coating. However, a useful coating may usually be formed in 10 minutes or less, and an extended time even of several hours does no harm.

Agitation during the coating operation maintains uniform temperature conditions and gives better coatings. It is also useful in avoiding the formation of gas pockets in curved or recessed parts of the article.

If the work is not completely clean there is apt to be unevenness and varying thicknesses of surface coating with consequent uneven coloration by subsequent dyeing. Defective contacts with individual pieces in processing a batch of articles may require their reprocessing. To remove the coating for reprocessing the article a 5 to 10 per cent hydrofluoric acid dip is most satisfactory. On immersion the coating rapidly dissolves, solution taking perhaps 15 seconds. There is then a vigorous evolution of gas as the acid reaches the metal. When this occurs the articles are removed and washed. Because of the stated etching it is frequently necessary to rebuff or repolish the article. When cleaned and washed, and if necessary repolished, the article is ready for reprocessing.

The anodic treatment described usually gives a coating of about 0.0005 inch thick. With a somewhat greater time of anodic treatment the thickness of coating may be 0.0015 inch or more. These thicknesses are sufficient for all ordinary purposes, and while somewhat thicker coatings may be secured the result is more attack on the underlying aluminum.

In coating, some of the metal goes into solution in the acid as aluminum sulfate and after a time the acid becomes saturated and deposits crystals. To dispose of this crystallized sulfate and keep down the temperature of the bath, it is usually expedient to keep a portion of the bath in cyclic circulation to and through a filter and cooling means and back to the bath. A leadlined pump may be used.

Some properties of a coating produced by the anodic treatment are as follows: It is a non-conductor of electricity when dry and

oiled; it is readily reactive with, absorbs and permanently holds organic dyes; it is resistant to wear; it stands buffing and takes a high polish; it withstands heating without lifting or breaking away from the metal; it binds paints, oils, enamels, lacquers and the like; it shows no definite crystalline structure under X-ray examination; and it is a coating of reasonable thickness rather than a film. The coating is apparently entirely non-crystalline or amorphous but, as stated, varies in character in different depths. The sub-microscopic porosity is of a type like that with "silica gels", the amount of internal surface being very great. This, together with the transparent nature of the coating, is an explanation of the bright and true colors which can be obtained in dyeing. In one particular coating about 0.00066 inch thick, the porosity represented about 40 per cent of the total film. The coating is resistant to heat, withstanding temperatures up to, say, 300° C., without shelling or cracking and without much loss of water. With well rinsed material, the amount of microscopic moisture given at 100° C., is very little. The rest of the H_2O is more permanently held. The coating is tolerably resistant to acids but loses sulfuric acid in alkaline liquids. It gives up sulfate to boiling water but two hours boiling with distilled water are required for completion of the action. Rinsed, dry material does not corrode in the air and with the pores plugged or filled, corrosion by sea water does not occur. As illustrating the adsorptive power of the coating material, it may be mentioned that on application of lacquers containing dyes, some of the dye sometimes migrates into the underlying coating.

When taken from the coating bath, the coating is well rinsed to free it of acid. It is then, usually, dried. It may then be baked. Baking makes it somewhat more porous and less adapted for taking up dye. Prior to drying and baking, various dips may be used to neutralize retained electrolyte or free acid. Coatings which are simply dried or baked, but not otherwise treated, are useful in some relations, as on aluminum pistons.

Where the coating is to be dyed, it is in general used wet, i. e., after rinsing and, in some cases, after a neutralizing dip. The rinsed, wet coating dyes readily but displays its own specific peculiarities in dyeing. In a general way, all dyes which can be used with an alumina mordant can be here used. Acid dye baths are not, in general, applicable; even those which are acid with acetic acid. In neutralizing dye baths, neutralization with sodium carbonate is better than neutralization with ammonia. The presence of ordinary salines employed in dye baths as "assistants", such as sodium sulfate, is not injurious. An addition of sodium chromate is often useful. In articles exposed to light, lightfastness of the dye is highly important; and for automobile finishes and the like, even with dyes ordinarily regarded as lightfast, the use of protective lacquers or varnishes, shutting out ultra-violet light is sometimes necessary. However, dyes which are really lightfast can be used.

Dyeing is done in the usual way with the usual baths and requires usually 30 minutes to an hour. Exhaustion of the bath is generally good. Articles to be dyed are suspended in the dye bath from aluminum rods or on aluminum racks or with aluminum wire. After dyeing, the article is rinsed and air-dried. In some cases, it is buffed after drying, using a standard white lime composition of the type used for nickel buffing. In so doing, the binder of the buffing composition, which is usually stearic acid or tallow, is taken up, more or less, in the pores. Sometimes, the dyed coating, after air-drying or oven drying, is further treated with fillers which may be liquid, waxy or solid. For instance, waxes of varying melting points or solutions of waxes in various organic solvents or slushes which can carry greases or resins into the body of the film, may be used. After such procedure, buffing is not usually resorted to, but the article is merely dried with clean rags and then polished by hand.

In the selection of a filler, the choice depends on the kind of resistance required of the treated article. A finished article with a coat that is required to contain foodstuffs, such as refrigerator trays, may be treated with a casein filler. A wide variety of chemical dips can be employed in lieu of casein. It is usual not to buff after a filler has been employed, as the work drags under the buffing wheel and sometimes is smeared, instead of being even in color. Where it is necessary to get a good finish after dyeing, buffing is resorted to without the colored piece being previously treated. The articles, after buffing, can be made impervious with certain oils and solutions. I have used molten lanolin and lanolin dissolved in benzol. I have also used petrolatum and paraffin. Beeswax and similar materials are very good.

Various kinds of decorative or ornamental effects are possible with the anodic sulfuric coating. Parts of an article may be coated, dyed, oiled, painted, varnished or lacquered, while other parts are left with their natural surfaces, or these other parts may be differently dyed, oiled, painted, varnished or lacquered.

Generally I cover the whole article with a coating; but in special cases I localize the coating, thereby producing special articles. For example, in aluminum cooking utensils it is desirable that the sides be polished metal to lessen radiation and cooling while it is desirable that the base be black or dark colored to facilitate heating on the stove. With

aluminum cooking utensils therefore I customarily stop off all the surface with celluloid, asphaltum base, paraffin or suitable stopping off material, except the bottom or the heat receiving surface. This I coat as previously described, dye with a black or dark dye and then fill with wax or the like. In heating the kettle or the like this wax customarily goes above its melting point but it does not ooze out or leave the article if the coating is properly made.

The present invention is applicable to any article of aluminum or its alloys. In the case of duralumin and other alloys containing silicon, the coating carries some silica, but its properties are about the same.

In addition to the cooking utensils mentioned, the present invention finds utility in application to automobile and aeroplane parts and accessories. Beautiful and permanent finishes can be given to sheet metal without the use of varnishes or lacquers. The sheet metal may be given a pebble or leather finish, then coated and finally dyed and filled. Radiators may be coated inside and outside; the inside coating being left undyed while the outside is dyed in a dark color to promote radiation.

Aside from its advantageous mechanical properties, the present coating owes most of its value to its highly developed adsorptive power; a power which enables it to take up and hold oils, coloring matters, etc. against withdrawal. I attribute this high adsorptive power in part to the large amount of fixedly contained SO_3; or basic aluminum sulfate as the case may be. This basic sulfate is in a form resisting action by cold water and it is extremely active as an adsorbent. In the article of the present invention, the fixedly held SO_3 may range between, say, 16 per cent and 23–24 per cent of the coating.

What I claim is:—

1. An article of aluminum or alloy thereof having formed thereon an integrally united coating containing Al_2O_3, SO_3 and H_2O, having a thickness of the order of a thousandth of an inch obtained by anodic oxidation of said article in a bath of sulfuric acid between 1.5 and 1.7 specific gravity and being of glassy hardness next the metal with lessened hardness toward the surface, said coating being resistant to water and to wear, minutely porous, adsorptive, capable of being buffed and polished and capable of being dyed with level appearance.

2. An article of aluminum or alloy thereof having formed thereon an integrally united coating containing Al_2O_3, SO_3 and H_2O, having a thickness of the order of a thousandth of an inch obtained by anodic oxidation of said article in a bath of sulfuric acid between 1.5 and 1.7 specific gravity and being of glassy hardness next the metal with lessened hardness toward the surface, said coating being resistant to water and to wear, minutely porous, adsorptive, and having its pores filled with impregnating matter.

3. An article of aluminum or alloy thereof having formed thereon an integrally united coating containing Al_2O_3, SO_3 and H_2O, having a thickness of the order of a thousandth of an inch obtained by anodic oxidation of said article in a bath of sulfuric acid between 1.5 and 1.7 specific gravity and being of glassy hardness next the metal with lessened hardness toward the surface, said coating being resistant to wear, minutely porous and adsorptive, being buffed and having its pores filled with oily impregnants.

4. An article of aluminum or alloy thereof having formed thereon an integrally united coating containing Al_2O_3, SO_3 and H_2O, obtained by anodic oxidation of said article in a bath of sulfuric acid between 1.5 and 1.7 specific gravity, said coating having a thickness of the order of a thousandth of an inch and being of glassy hardness next the metal with lessened hardness toward the surface, said coating being resistant to wear. minutely porous, adsorptive and being dyed and buffed.

5. An article of aluminum or alloy thereof having formed thereon an integrally united adsorptive coating containing Al_2O_3 and H_2O and an amount of SO_3 exceeding 16 per cent of the weight of the coating as a whole.

6. An article of aluminum or an alloy thereof having formed thereon an integrally united adsorptive coating having the composition and properties characteristic of an anodic deposit upon the metal in a sulfuric acid electrolyte having a specific gravity between 1.5 and 1.7.

7. An article of aluminum or alloy thereof having an integrally united adsorptive SO_3—containing coating deposited thereon by making the article an electrolytic anode in sulfuric acid of about 65 per cent strength, said coating being dyed.

In testimony whereof, I have hereunto affixed my signature.

HELMER BENGSTON.