

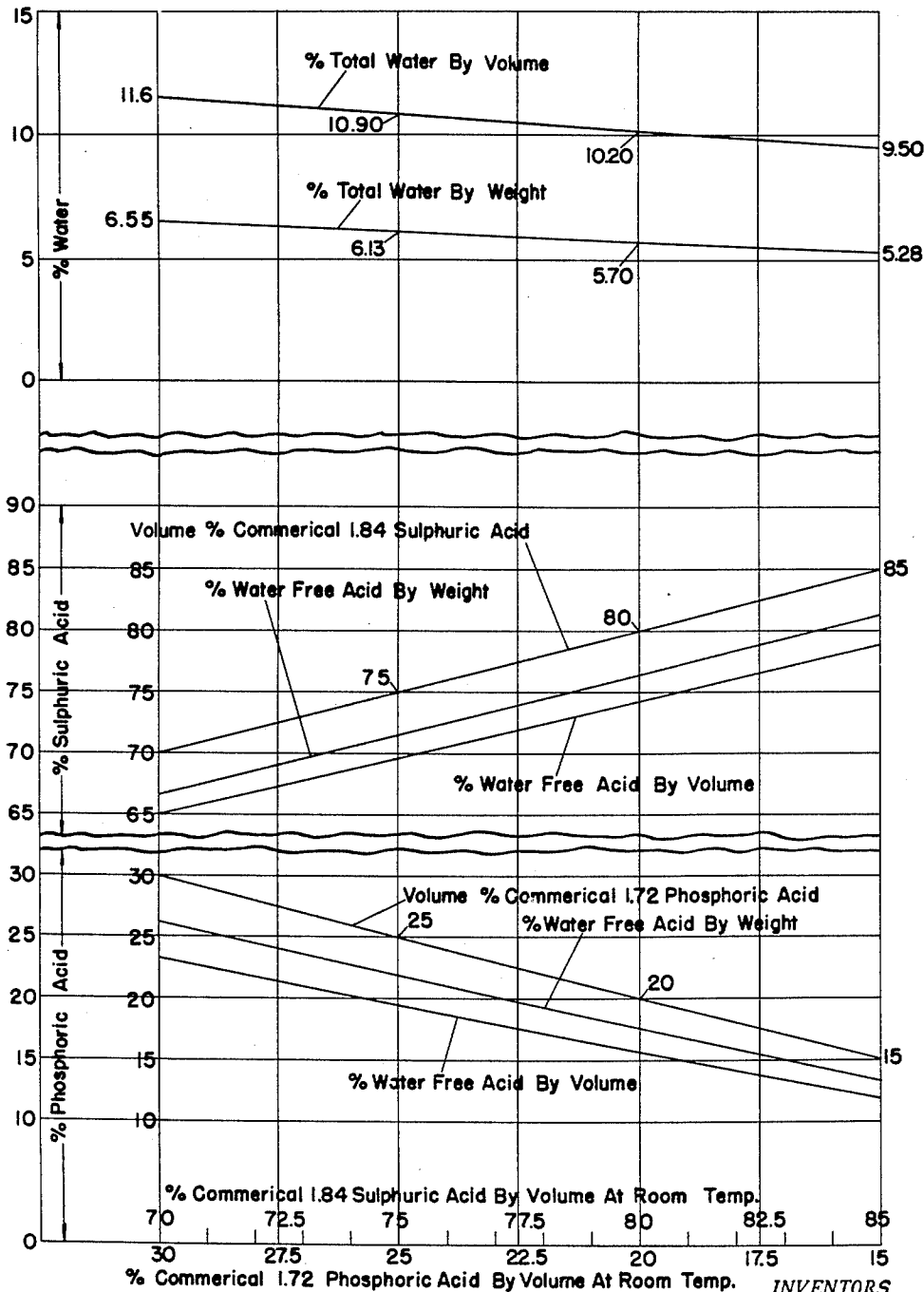
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CHEMICAL BRIGHTENING AND ELECTROLYTIC POLISHING OF ALUMINUM

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CHEMICAL BRIGHTENING AND ELECTROLYTIC POLISHING OF ALUMINUM

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The desirability of providing a bright surface finish on aluminum has long been recognized. Various types of chemical and electrolytic treatments have heretofore been proposed, but, so far as we have been able to determine, none has yet succeeded in producing consistently good results on aluminum and the alloys thereof. Furthermore, the brightening of aluminum by successive chemical brightening and electrolytic polishing operations, has always heretofore required, so far as we know, separate chemical brightening and electrolytic polishing baths of entirely different character

The principal object of this invention is to provide a chemical bath which is composed of relatively inexpensive ingredients, is substantially non-fuming when out of contact with aluminum, is stable so that it is readily maintained at proper strength and composition, and is capable of being used either as a brightening bath or as an electrolytic polishing bath or as both.

Another important object is to provide a chemical bath which, when used as a chemical brightening bath or as an electrolytic polishing bath or as a combination chemical brightening and electrolytic polishing bath, gives extremely good surface improvement results on aluminum and on a wide range of its alloys.

Further objects are to provide a novel chemical brightening process, a novel electrolytic polishing process and a novel combination process.

Our invention resides first in formulating a novel bath having, as its primary ingredients, relatively large and small quantities of commercial sulfuric and phosphoric acids respectively and in discovering that a bath of this character may be used as a chemical brightening or as an electrolytic polishing bath or as a combination chemical brightening and electrolytic polishing bath.

The figure is a graph showing the range of acid mixtures in baths formulated in accordance with our invention and the amount of water in each of said mixtures.

For the sake of clarity, the three processes utilizing one and the same bath are dealt with first.

CHEMICAL BRIGHTENING PROCESS

The steps of our chemical brightening process may be outlined as follows:

- (1) Provide a clean or dirty aluminum article;
- (2) Dip the article into a hot chemical bath, formulated in accordance with our invention;
- (3) Remove the article from the bath and allow to cool;
- (4) Rinse the article in water; and
- (5) Apply a protective film to the article.

The aluminum, provided for treatment in accordance with this invention, should be clean but it may be dirty provided the dirt is of a character such that it comes off easily. Thus aluminum coming from a fresh buffing operation may be used without any cleaning operation since fresh buffing dirt comes off very readily in the chemical bath. Where aluminum has been buffed and allowed to stand, the buffing dirt tends to stick to the aluminum and

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this will interfere with the practice of this invention unless the dirt film is removed.

The aluminum is dipped into a chemical bath, formulated in accordance with our invention as hereinafter described. It remains in that bath for a period of time ranging from one minute, if the surface of the aluminum is smooth, up to three to five minutes or more if the surface of the aluminum is rough. Mild agitation of the bath is desirable. This can be accomplished by gently moving the parts to be brightened or by air. The chemical bath temperature should be maintained between 230 and 300° F. (110–148.9° C.) but the preferred temperature range is between 250 and 260° F. (121.1–126.4° C.). When the aluminum is removed from this bath, it will be covered by a layer of viscous material ranging in color from creamy white to creamy white yellow. This layer should not be removed before the rinsing step since it tends to prevent any etching of the aluminum.

When the layer-protected aluminum is removed from the bath, it should be allowed to stand for a period sufficient to permit it to drain and cool. This period ranges from ten seconds upwardly but it need not be of great duration. Ordinarily ten to twenty or thirty seconds will be enough. But, when desirable or necessary, it may be allowed to stand for longer periods.

The aluminum is rinsed or washed in a bath of warm or cool tap water, room temperature being preferable. The rinsing or washing action normally will take thirty to sixty seconds and should be vigorous enough to insure the removal not only of any free acids but also of the compounds which may have been formed or deposited on the aluminum such as sulfur, aluminum sulfate, and aluminum phosphate, etc. The rinse water preferably is agitated or circulated as by flowing it continuously from a tap through the rinsing bath to an overflow leading to the sewer. There is apparently no brightening action after it is removed from the brightening bath. If the work is cooled before rinsing, there will be no etching action during the rinsing step. Etching is usually evidenced by whitish spots. The occurrence of etching, during rinsing, appears to be a function of the accumulation or concentration of acid in the rinsing bath and the temperature of that bath. As the acid concentration or the temperature of the rinsing bath increases, the tendency to etch increases. The rinsing step may be repeated one or more times if desired.

The aluminum may now be dried. Preferably a protective film is applied thereto either by conventional anodizing before drying or by lacquering after drying.

ELECTROLYTIC POLISHING PROCESS

This process is identical with the chemical brightening process except for the dipping step 2 and the transfer step 3. In the electrolytic dipping step, the aluminum is dipped into the chemical bath, which now functions as an electrolytic bath, for a period of time ranging from thirty seconds to two minutes. The aluminum functions as the anode of the chemical-electrolytic bath and a current flow should be maintained in that bath with a current density ranging, in amperes per square foot of surface area of aluminum, from 40 with a low water content in the bath to 150 with a high water content, the bath voltage being from 8 to 15 volts. The bath temperature ranges from 200 to 250° F.

Upon removal from the chemical-electrolytic bath, the aluminum should be transferred to the rinsing bath immediately or promptly to avoid etching. This is due to the fact that the protective layer, which is obtained in the chemical brightening process, is either eliminated or substantially reduced by the electrolytic polishing process. Cooling before rinsing is not necessary or even desirable. The flow of bath water should be such as to minimize

the accumulation of acid therein and maintain the temperature under a desired maximum or both.

COMBINATION PROCESS

The steps of this process are the same as the electrolytic polishing process except for step 2. In step 2 the aluminum is dipped into the chemical bath for chemical brightening purposes as in the brightening process above outlined and under the same conditions except that the temperature of the bath is now maintained in the range of 230 to 250° F. Thereupon the current is turned on in that bath to practice step 2 of the electrolytic process. The article may, of course, be transferred to a separate electrolytic polishing bath which may be, and preferably is, of the same composition as the chemical brightening bath, but, in this event, the temperature ranges may be 230–300° F., for brightening and 200–250° F. for polishing. If transferred, the transfer time between the chemical brightening bath and the electro polishing bath is unimportant because of the protective layer produced during chemical brightening. After the electrolytic polishing step, rinsing should follow immediately as before.

COMPOSITION OF BATHS

While our chemical brightening bath is maintained at a temperature ranging from 230° F. to 300° F. and preferably between 250° F. and 260° F., its room temperature composition essentially comprises:

- (1) Commercial phosphoric acid ranging, in volume, from 15% up to 30%, 25% being preferred;
- (2) Commercial sulfuric acid ranging, in volume, from 85% down to 70%, 75% being preferred; and
- (3) Silver salt ranging, by weight, from 0.001% to 0.10%.

The room temperature composition of our combination bath is the same but, in our electrolytic polishing bath, the silver salt may be omitted.

The percentage values given above are approximate; hence should be read as not substantially below the lower or above the higher limits stated.

The various oxyacids of phosphorus may be regarded as derived, theoretically at least, by hydration of the various oxides of phosphorus. Some of the oxyacids of phosphorus, derived from lower oxidation states of phosphorus, decompose upon heating with the resultant formation of the higher oxyacids of phosphorus, and, where such decomposition is not objectionable, they may be used in our compositions. We prefer to employ orthophosphoric acid, but pyrophosphoric acid and metaphosphoric acid may be employed. The oxyacids of phosphorus may be employed as the soluble acid salts in whole or in part. For example, in place of ortho phosphoric acid, the mono alkali metal phosphate may be employed. Other alkali metal salts of ortho-phosphoric acid may be employed provided enough excess sulfuric acid is present to avoid the depletion of sulfuric acid in the bath. The water soluble salts used should not be those which will react in the bath to form insoluble compounds.

While the silver salt is mentioned above as an essential ingredient in our brightening and combination baths it is not essential therein when treating the following wrought aluminum and/or wrought alloys; (1) high purity aluminum 99.80% Al, (2) commercially pure aluminum (2S alloy), (3) aluminum alloys containing magnesium silicide as the principal hardening agent (63S alloy with a nominal content of 0.70% magnesium and 0.45% silicon and 61S alloy with a nominal content of 1.00% magnesium and 0.60% silicon), (4) aluminum alloy containing 1.25% manganese (3S alloy) and (5) aluminum alloys containing less than 0.5% magnesium as the principal hardening agent. All percentages herein given are by weight.

However the addition of a silver salt makes it possible to secure excellent brightening results consistently when

treating aluminum alloys containing magnesium from 0.5% to 5.0% by weight. An example of an alloy would be C57S which contains a nominal magnesium content of 1.0%. Since the composition of aluminum articles to be treated may vary from day to day in many commercial operations, the silver salts should be and preferably are incorporated in the bath for all treatments. These salts may be silver nitrite, silver nitrate or silver cyanide or their equivalents.

THE FIGURE

The figure, for clarity, is based on the assumption that the combined volumes of commercial phosphoric and sulfuric acids make up 100% of the bath volume; hence the silver salt addition is based on the weight of the commercial acid contents of the bath as a whole. The figure also assumes that the specific gravities of commercial sulfuric and phosphoric acids are 1.84 and 1.72 respectively and it gives the commercial acid contents of the bath in sulfuric to phosphoric volume ratio form ranging from 70/30 to 85/15. This figure shows, for each volume percentage of commercial acid employed, at room temperature, the corresponding volume and weight percentage of each acid on a water-free basis and the corresponding volume and weight percentage of the total water content in the bath.

Furthermore it will be understood that the differences between the volume percentage of commercial acid and the corresponding volume and weight percentages of the same acid on a water-free basis, will give the water content of each acid in terms of both volume and weight percentages. But all of these percentages obtain under room temperature conditions which are assumed to be 72° F.

WATER CONTENT

Under operating conditions, at temperatures above 212° F., the water content will be lower than that shown in Figure 1 since water will boil off until an equilibrium condition is reached depending upon the operating temperature employed and the humidity of the atmosphere. This reduction in water content is very desirable with smooth surfaced aluminum because the lower the water content, the better and more consistent are the results. The addition of water to the bath is not prohibited, but, it should be avoided since it increases the tendency of aluminum in each bath to etch rather than to brighten and increases the current flow in the electrolytic bath. Accordingly the recommended procedure is to bring the bath up to the operating temperature and preferably maintain it at that temperature until the water content stabilizes before instituting the regular use of the bath.

With rough surfaced aluminum, a higher water content is preferred but, when used, it must be carefully controlled because of the increased tendency to etch.

BUFFING TREATMENT

Buffing of an article before it is either brightened or polished or both, is usually not necessary because our brightening or polishing bath has a tendency to level off shallow scratches and the drawing marks characteristic of shallow drawing operations. Even deep scratches can be removed with a longer dipping time but, in some instances at least, it will be more desirable to buff out deep scratches.

TEMPERATURE

As the operating temperatures of the bath progressively falls toward the lower limit, the dip time required to produce optimum results progressively increases. Progressively below the lower temperature limit, the tendency to etch progressively increases. As the operating temperature progressively rises toward the top limit, the dipping time progressively decreases. As this temperature progressively rises above the top limit, the brightening or polishing action progressively becomes more sen-

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sitive. Where the bath is too sensitive, the first part of an article entering the bath will be overtreated if the last part entering the bath receives the proper treatment. Overtreatment generally results in a surface which may be described as an "etched" surface.

BATH RATIO AND MAINTENANCE

In the operation of the bath, both phosphoric and sulfuric acid are lost through chemical reaction. Since the sulfuric acid loss proceeds at a rate faster than the phosphoric acid loss, the progressively higher sulfuric to phosphoric acid ratios enable the bath to be operated over progressively longer periods of time before replenishment is required. This ratio, however, should not be permitted substantially to exceed the top limit of 85/15 because there is a progressive increase in the tendency of the bath to etch the aluminum. Neither should it be permitted to fall substantially below the lower limit of 70/30 because of the progressive decrease in the production of good results. Thus, as the ratio closely approaches 65/35, the results become too inconsistent to permit a satisfactory continuance of either the brightening or the polishing operation or both. Accordingly, when the bath becomes depleted, it may be restored by titrating for each acid and then adding the requisite quantities required to bring the bath up to the desired acid ratio.

REACTION FUMES

We are unable to explain completely, the mechanism of the reactions occurring in either or both operations. When heated but not in use, the bath does not produce fumes or odors to any appreciable extent. When aluminum is immersed in the hot bath, there is a noticeable odor of sulfur dioxide and hydrogen sulfide and some sulfur formation, which indicates the sulfuric acid is being reduced. However, sulfur does not settle out to any substantial extent but apparently is reoxidized.

REFLECTIVITY

Our invention will produce highly reflective surfaces on mill finish wrought aluminum alloys. As an example, an unbuffed mill finished aluminum sheet (CS7S alloy) was divided up into specimens numbered 1 to 3 and 4* to 6*. Specimen 1 was left in the mill finished condition. Specimen 2 in the mill finished condition was chemically brightened. Specimen 3 in the mill finished condition was chemically brightened and electro-polished. Specimens 4* through 6* were wire brushed. Specimen 4* was left in the wire brushed condition. Specimen 5* was chemically brightened after wire brushing. Specimen 6* was chemically brightened and electro-polished after wire brushing. All samples were subjected to reflectivity measurements on a previously calibrated Gardner Hazemeter.

The results are shown in Table I wherein: "Chem. B" designates chemically brightened; "Combined" designates chemically brightened and electrolytically polished; and "T" and "S" respectively designate total and specular reflectivity.

Table I

Specimen Number	Control		Chem. B		Combined	
	T	S	T	S	T	S
1	66	18				
2			87	77		
3					87	80
4*	71	4				
5*			87	75		
6*					87	77

In addition to producing highly reflective surfaces on wrought aluminum alloys our invention will also produce attractive surfaces on untreated cast aluminum alloys. In these cases, however, since the original surface roughness

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is considerably greater in addition to being more porous, than on wrought products, the final appearance is generally one of high diffuse reflectivity rather than specular reflectivity.

Having described our invention, we claim:

1. A method for surface brightening and polishing an article composed of a metal selected from a group consisting of aluminum and its alloys comprising: providing a bath consisting essentially of sulfuric acid, phosphoric acid and water, corresponding, in nature and amount, at room temperature to a mixture of commercial sulfuric and phosphoric acids in room temperature volume ratios ranging from 70% commercial sulfuric over 30% commercial phosphoric to 85% commercial sulfuric over 15% commercial phosphoric so that the total water-free acid content of the bath ranges from about 88½% to about 90½% of the total volume of the bath; heating the bath to a temperature ranging from about 200° F. to about 300° F.; and dipping the article into the heated bath for surface brightening purposes.

2. The method of claim 1 wherein: the bath is heated to a temperature not substantially lower than 230° F.; and the dipping step includes dipping the article into the bath, without an electric current flowing through the bath, for chemical brightening purposes.

3. The method of claim 1 wherein: the bath is heated to a temperature not substantially higher than 250° F.; and the dipping step includes dipping the article into the bath, with an electric current flowing from the article through the bath, for electrolytic polishing purposes.

4. The method of claim 1 wherein: the bath temperature ranges from about 230° F. to about 250° F.; and the dipping step includes dipping the article into the bath without an electric current flowing through the bath for chemical brightening purposes and thereafter causing an electric current to flow from the article through the bath for electrolytic polishing purposes.

5. The method of claim 1 including: providing another bath substantially duplicating the first mentioned bath; maintaining one bath at a temperature not substantially below 230° F. and the other at a temperature not substantially above 250° F.; and thereafter performing the dipping step by dipping the article into said one bath without an electric current flow therethrough for chemical brightening purposes and into said other bath with an electric current flowing from the article through the bath for electrolytic polishing purposes.

6. The method of claim 1 wherein: the providing step includes providing a bath having, as another component, a relatively small amount of a silver salt.

7. The method of claim 6 wherein: the bath is heated to a temperature not substantially below 230° F.; and the dipping step includes dipping the article into the bath without an electrical current flowing through the bath for chemical brightening purposes.

8. The method of claim 6 wherein: the bath is heated to a temperature not substantially above 250° F.; and the dipping step includes dipping the article into the bath with an electric current flowing from the article through the bath for electrolytic polishing purposes.

9. The method of claim 6 wherein: the bath is heated between about 230° F. and 250° F.; and the dipping step includes dipping the article into the bath without an electric current flowing through the bath for chemical brightening purposes and thereafter causing an electric current to flow from the article through the bath for electrolytic polishing purposes.

10. The method of claim 6 including: providing another bath substantially duplicating the first mentioned bath; maintaining one bath at a temperature not substantially below 230° F. and the other not substantially above 250° F.; and performing the dipping step by dipping the article into said one bath without an electric current flow therein and into said other bath with an

electric current flowing therein from the article through said other bath.

11. A composition for use at an elevated temperature in surface brightening and polishing an article composed of a metal selected from a group consisting of aluminum and its alloys comprising: a bath consisting essentially of sulfuric acid, a material selected from the group consisting of phosphoric acid and acid salts thereof, and water, corresponding in nature and amount, at room temperature and on the basis of equivalent phosphoric acid, to a mixture of commercial sulfuric and phosphoric acids in room temperature volume ratios ranging from 70% commercial sulfuric over 30% commercial phosphoric to 85% commercial sulfuric over 15% commercial phosphoric so that the total water-free acid content of the

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bath ranges from about 88½% to about 90½% of the total volume of the bath.

12. The composition of claim 11 including: a relatively small amount of a silver salt.

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