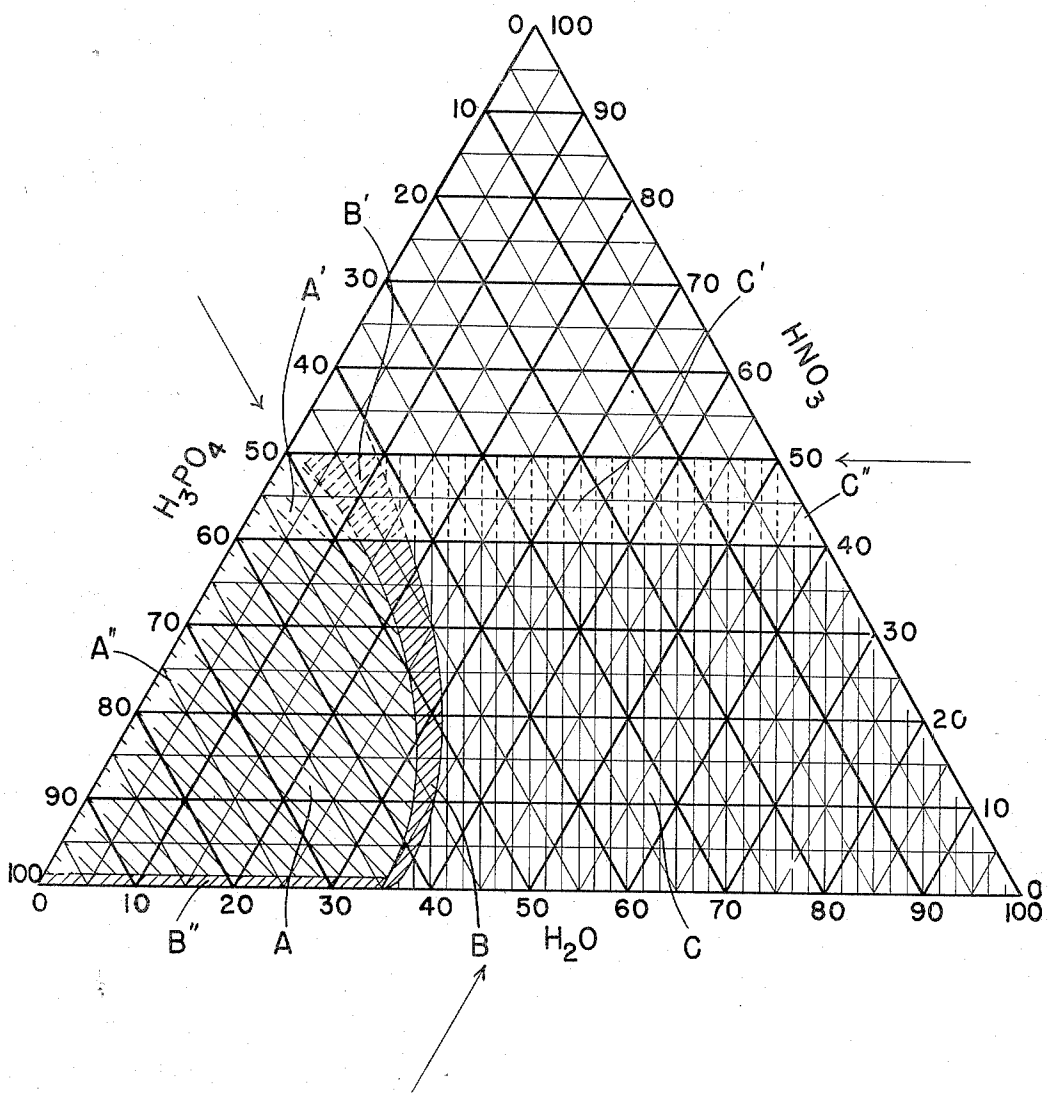
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SURFACE TREATMENT OF ALUMINUM AND ITS ALLOYS

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SURFACE TREATMENT OF ALUMINUM AND ITS ALLOYS

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12 Claims. (Cl. 41—42)

This invention relates to the surface treatment of aluminum or its alloys and has particular reference to the chemical polishing or chemical buffing thereof.

This application as a continuation of my application Serial Number 13,291, filed March 5, 1948, now abandoned, which application was a continuation of the application of myself and Richard L. Barwis, Jr., Serial No. 700,024, filed September 28, 1946, now abandoned.

Various attempts have been made to secure bright or highly reflective surfaces on aluminum or its alloys by means of electrochemical treatment as an alternative to mechanical buffing. Such procedures have produced fairly satisfactory results and have generally been superior to mechanical buffing and consequently are being used more and more to secure bright or reflective surfaces. Mechanical buffing has various limitations particularly in that it is impractical to apply it without great difficulties, involving individual and special handling of work consisting of smooth or intricately shaped pieces.

Electro-polishing, or electro-buffing as it is sometimes called, is also frequently impractical because of the difficulty of racking small or oddly shaped pieces and because the electro-chemical action does not properly take place in substantially depressed or recessed areas. Furthermore, electro-polishing is expensive because high current densities are required which necessitate the use of large generators or rectifiers to supply the necessary current. The high current densities require heavy cross-sections of rack materials to carry the required currents so that the amount of work which may go into a given volume of bath is limited.

In accordance with the present invention there is provided a treatment for aluminum or its alloys involving in its simplest form merely immersion in a bath of the articles to be treated though, if desired, electrochemical action may be provided in accordance with a modification of the invention. By this treatment, with minor changes in each case, there may be produced highly reflective specular surfaces, diffuse surfaces of high reflection characteristics, or white matte surfaces characterized by a very high reflectivity for light. The time of immersion involved may be very short, of the order of a fraction of a minute. The metal surfaces following the treatments become passivated and are, therefore, rendered more corrosion resistant as well as forming excellent bases for subsequent treatments. Furthermore, the solutions used have long life and are, therefore, economical.

In order to make clear the practices in accordance with the invention there may first be defined certain terms as applied to surface finishes in the present description.

By specular finish there is meant herein a uniform mirror-like surface which is specularly reflective, i. e., in which objects may be viewed by reflection with the resulting appearance of images similar to the results secured by viewing the objects in a mirror.

By a matte finish there is meant a smooth white or

gray-white uniform finish highly reflective of light but not mirror-like in the sense of giving rise to images by reflection.

By diffuse finish there is meant a finish intermediate between the foregoing which appears metallic and smooth and approaches a specular finish in giving rise by reflection to images which, however, are somewhat blurred. The term "diffuse," as will be clear from the foregoing, is thus used to define an intermediate type of finish between specular and matte. As will be evident hereafter these finishes constitute a series without sharp demarcation from each other but the terms will be useful in describing the various treatments in accordance with the invention.

In common, all of these finishes are macroscopically uniform and smooth, i. e., by the unaided eye no nonuniformity may be detected. The matte finish, when rubber by the fingernail, gives a sense of producing slightly more friction than the specular finish but nevertheless gives no sensation such as is obtained in running the fingernail over even the finest cut files. Under the microscope at a magnification of one hundred times the matte surface exhibits a brilliant appearance of very fine evenly distributed and closely arranged rounded polished pits, which pits appear only in comparatively limited numbers in the specular finish and in intermediate numbers in the diffuse finish. In the two latter cases, under the magnification stated, the regions between the pits are smooth and specular.

As will be apparent hereafter the procedures constituting the present invention may be carried out to produce all three types of finishes with minor changes in compositions of the treating mixtures and the circumstances of the treatment.

In order to make clear the processes here involved references may be had to the accompanying drawing which illustrates in a triangular diagram the characteristics of various bath mixtures when applied to the treatment of 52S aluminum alloy at temperatures in the vicinity of the boiling point of the mixtures used, the temperature being understood to be 230° F. where the boiling point of the mixture at atmospheric pressure exceeds this temperature.

The triangular diagram relates to a three-component mixture of phosphoric acid H_3PO_4, nitric acid HNO_3 and water. The area A represented by hatching running from upper left to lower right represents the mixtures of these three components which, at the temperatures stated, will produce a specular finish on 52S alloy using an immersion period ranging from twenty seconds up to several minutes. It may be here remarked that the time of immersion in any case is not particularly critical. The minimum time depends largely upon the original condition of the surface being treated. If the surface is smooth to the extent normally characteristic of rolled aluminum alloys then an immersion time of twenty seconds may suffice to produce removal of irregularities such as superficial scratches, pores and other surface imperfections with a resulting specular finish. A longer time of immersion may be required for smoothing or evening the surface to a specular finish, if the surface scratches or mars are more than superficial. On deep scratches, however, unless a large amount of metal may be removed, it is more practical to take these imperfections out by some other method, such as grinding or polishing mechanically prior to treatment by this process. An extended period of immersion will, in general, produce no detrimental result so far as surface finish is concerned though a minimum period of immersion should be used if a minimum degree of solution of the work should occur. Excessively long periods of immersion may result in detriment to the finish due prob-

ably to uneven solution rate occasioned by non-uniformity in the alloy. Generally speaking, periods ranging from about twenty seconds to three minutes will suffice for average work. If the surface is preliminarily mechanically polished or buffed the treatment in the solution will result in extreme brilliance of finish and a minimum time of immersion, for example, a few seconds, will suffice.

The lower boundary of the region A approaching the line of zero content of nitric acid corresponds approximately to one-half percent of nitric acid. A good specular finish appear to require some nitric acid even though the quantity may be one-half percent or less.

It will be noted that in the regions indicated at A' and A'' the hatching is broken, these regions being respectively above 40% content of nitric acid and below a 2½% content of water. The regions thus indicated are considered impractical from a commercial standpoint. The region A' represents one in which the rapidity of action on the work is so great as to be difficult to control, clouds of nitrogen oxides being evolved making the operation difficult to carry out with safety to the workmen. Furthermore, a content more than 40% nitric acid results, at the most desirable temperatures of operation, in violent boiling of the nitric acid from the mixture. Since results are equally well obtainable with much lower concentrations of nitric acid it is generally desirable to operate in the lower portion of the region A when a specular finish is desired.

The region A'' represents one in which the solution is excessively viscous with the result that when the work is withdrawn from the bath it will carry out an excessive amount of the mixture. Consequently, this region is also generally to be avoided in practice. It will, of course, be understood that under laboratory conditions the entire region A, including the regions A' and A'', are useable.

The region B represents the compositions of the bath which will give rise to diffuse finishes, i. e., in this region the specular reflectivity decreases and shades off toward the matte finish described above. The broken hatching indicated in the portion B' of this region above the 40% nitric acid content again represents a region of rapid solution, fuming, and excessive boiling off of nitric acid when the operation is carried out at temperatures around 230° F.

It will be noted that the region B has a portion indicated at B'' below the region A and representing a reduction in the nitric acid content below about one-half percent. When the nitric acid content is below this percentage or when it is completely absent a diffuse finish results down to a concentration of phosphoric acid of about 65%. If a diffuse finish is desired this region is available for operation inasmuch as the production of a diffuse finish can be controlled by limitation of the quantity of nitric acid or lowering the temperature. As pointed out hereafter the boundaries of the regions are by no means sharply defined so that it is difficult to insure a diffuse finish in the narrow upwardly extending portion of region B corresponding to higher percentages of nitric acid.

The region C represents the region of production of matte finishes. The portion C' of this region again represents rapid solution, fuming, and excessive boiling off of the nitric acid. While the various hatched areas are extended only to the line representing 50% nitric acid, it will be understood that higher contents of nitric acid may be used resulting, in general, in the formation of matte finishes, with about 60% nitric acid as the upper limit determined by extreme rapidity of the solution of the work. From a practical standpoint, however, the nitric acid should generally be limited to less than 40%.

The line indicated at C'' corresponding to about 1% phosphoric acid represents the right-hand boundary of the region C. As little as 1% phosphoric acid may be used in the production of the matte surface.

The diagram which has been illustrated represents as stated the conditions for the treatment, specifically of 52S alloy, with mixtures of phosphoric acid, nitric acid and water at temperatures ranging from about 210° F. to 230° F. It will be understood that the boundaries between the regions A, B and C are not sharply defined. Working, for example, in the region A close to the boundary between it and the region B there can be no absolute certainty of securing a good specular finish which may instead tend to become somewhat diffuse. Accordingly, if a good specular finish is desired the operation should be carried out well away from this boundary. Similarly, if a good matte finish is desired the operation should be carried out in the region C well away from the boundary between the regions B and C. If the high temperatures indicated are used, a diffuse finish can be obtained with certainty only in the region B''. Actually the diffuse finish is best secured with certainty as hereafter pointed out.

As an example of a bath giving a good specular finish there may be cited one comprising 100 gallons of 75% phosphoric acid and 7 gallons of 65% nitric acid, to be used at 230° F. with a two minute immersion.

So far the discussion has been directed to treatment of 52S alloy with mixtures of phosphoric and nitric acids and water at temperatures ranging from about 210° F. to 230° F. Variations of conditions and alloys being treated may now be described using the foregoing as a basis.

In the treatment of pure aluminum and such alloys as 2S, 3S, 53S, "Alclad" and "Pureclad" the conditions and results may be essentially the same as in the case of treatment of 52S alloy.

Copper alloys such as 17ST and 24ST require operation at the highest temperatures for best specular and matte results. With these copper alloys it is generally desirable to effect treatment as described to produce a smoothing of the surface, this being followed by a dip in nitric acid or other copper removing solution followed by a second treatment in the finishing solutions described above. The reason for this is that the first treatment will frequently result in the formation of a smut apparently due to the copper content of the alloy, which smut is removed by the dip in nitric acid. A further short treatment in the phosphoric-nitric acid-water mixture will then generally give fairly good results, the cycle being repeated if necessary. Usually, however, the specular finishes are somewhat inferior to those obtained on pure aluminum or aluminum alloys which do not contain substantial amounts of copper, the copper alloys generally tending toward the production of diffuse finishes under conditions which, when copper is absent, will produce specular finishes. When the highest degree of reflectivity is desired it is preferable to treat such alloys as 52S, 2S, or 3S, although many other alloys may be treated with substantially equally good results.

In the treatment of silicon alloys such as used for castings, specular finishes are generally impossible due to inherent porosity, alloy composition, and the formation of silicon on the alloy surfaces; nevertheless excellent matte effects, approaching diffuse, are obtainable. The silicon exposed by the treatment may be readily removed by brushing or by chemical treatment.

The temperatures used may range downwardly to about 200° F. without substantial change in the results obtained, i. e., the regions of the diagram illustrated in the drawing holding without substantial change for such temperatures. Below 200° F., however, the region A shrinks from the standpoint of production of specular finishes and in the region illustrated at A in the diagram either specular or diffuse finishes are obtained until the temperatures drop to about 160° F., the particular finish, below 200° F., depending upon the alloy. Accordingly, diffuse finishes are best obtained as a practical matter by operating in the region A between 160° F. and 200° F., the transition from specular finish to more and more diffuse finish with various alloys occurring as the temperature is lowered. At such lower temperatures the region C still represents

the region of formation of matte finishes. As the temperature is lowered the rapidity of action decreases and a higher minimum period of immersion is necessary to secure evening of the original finish of the work. Generally, therefore, for commercial production it is desirable to use as high temperatures as possible consistent with the production of the required results. Below about 150° F. down to and including ordinary room temperatures all three regions lead to the production of matte finishes.

In accordance with the foregoing, the aluminum or aluminum alloy is subjected to the action of a mixture including as its essential constituents approximately 45% to 98% of free phosphoric acid, approximately 2% to 35% of water, and approximately ½% to 50% of free nitric acid, said action taking place at a temperature in the range from 160° F. to the boiling point of said mixture. For bright reflecting surfaces the temperature should be at least 200° F. Brightening results are obtained using phosphoric acid and water alone when the mixture contains at least 65% of free phosphoric acid, with the mixture used at a temperature in the range from 150° F. to the boiling point of said mixture.

So far there has been considered treatment in solutions containing only phosphoric acid, nitric acid and water. The phosphoric acid content may be achieved by using the various orthophosphoric acid solutions on the market or by using equivalent quantities of meta or pyro phosphoric acids. The foregoing discussion, however, applies where the solutions used are such that the equivalent percentages of phosphoric and nitric acids may be said to be present in the total solution. For example, solutions may be made up of phosphoric acid, water and nitrates. In such case some of the phosphoric acid may be regarded as liberating nitric acid from the nitrates so that the solution may be calculated as having particular equivalents of free phosphoric acid and free nitric acid. On the basis of such calculations the diagram still applies, the indicated regions giving rise to the specified finishes. Similarly, nitric acid may be used together with phosphates such as monosodium and disodium phosphates to give equivalent results. It will be understood, accordingly, that when percentages of phosphoric and nitric acids are referred to in the present specification and in the accompanying claims that there are to be understood the equivalent quantities of phosphoric and nitric acids such as may be regarded as present in the solutions though obtained from phosphates or nitrates in the presence of acids.

The active constituents of the mixtures are essentially phosphoric acid and, where present at all, nitric acid, whether added in the free state or liberated equivalently in the solutions. It has been found that usually the additions of other constituents, including acids, compatible with the acids do not adversely affect the operations of the solutions so that such other materials may usually be considered as inert and merely replacing certain amounts of water. Specifically, the addition of sulphuric acid in small amounts is harmless and not advantageous in chemical polishing or buffing as described above. Large amounts of sulphuric acid, however, are to be avoided because they tend to slow down the reaction.

Sulphuric acid is advantageous, however, when the solutions described are used for electropolishing with the work forming the anode. In such operations the sulphuric acid increases the conductivity of the electrolytic bath and for this purpose sulphuric acid may be added in excess of the quantities desirable for our regular chemical polishing or buffing in which equivalent quantities might slow down the operation to an excessive degree. While the solutions described above with or without the addition of sulphuric acid may be used for anodic polishing no particular advantage is found to result from the use of electric current and from the practical standpoint this involves merely the unnecessary increase of expense of equipment, requiring either a generator or a rectifier. When used for electropolishing the baths are desirably operated at 160° F. to 180° F.

The finishing operations in all cases involve the solution of the aluminum and other constituents of the alloys. The lives of the various baths, however, are not appreciably affected until the aluminum phosphate content becomes quite high, for example, in excess of 50%. It has been found, for example, that a bath may be used until the aluminum phosphate content is so high that upon cooling the bath solidifies. If it is again heated so as to resume a liquid condition it may be utilized for finishing purposes.

The baths herein referred to effect degreasing and consubsequently it is not absolutely essential to degrease the work before treatment. Nevertheless, it is desirable to effect degreasing in the usual fashion to prevent deterioration of the baths by carrying into them grease from the work. Where extremely brilliant specular finishes are desired, preliminary mechanical polishing is advantageous.

When work is treated and removed from the bath it will, of course, carry with it some solution wetting its surface. When operating at high temperatures the solution dries very quickly on the surface of the removed work producing a coating thereon. This coating, however, may be completely removed by rinsing in water, whereupon the desired finish appears unmarred upon the work.

The various finishes produced in accordance with the invention are particularly adapted to further treatments. If aluminum or its alloys are mechanically polished and then anodized there is usually a loss of luster due to the etching action which occurs in anodizing. When, however, chemical polishing or buffing is carried out as described above and the resulting finishes are anodized, the original brilliance or finish is substantially retained. Even without anodizing the finishes resulting from the above treatments seem to be retained for longer periods than finishes obtained by other processes, with the possible exception of electrochemical processes.

The results secured by the anodizing or other oxide coating of the finishes produced by the methods given above constitute part of the present invention. The anodizing may be carried out in any of the conventional fashions using alternating current or direct current and acid or other electrolytes. The anodizing or other form of surface treatment may be followed by the conventional subsequent treatments generally used in connection with anodizing, such as dyeing, sealing, or other after treatments.

The fact that the finishes maintain themselves upon anodizing gives rise in particular to excellent finishes when the anodizing is followed by dyeing, sealing or other after treatment in the usual fashions. If the finish is specular, brilliant colored surfaces will result; if the finish is matte, dyeing or colored sealing produces beautifully colored opaque surfaces.

Treatment to produce matte surfaces produces on aluminum and its alloys white surfaces which are superior to those secured by treatment with caustic in conventional fashion. As contrasted with the caustic treatment which will produce a good white only on copper alloys the present processes produce excellent white matte surfaces on any aluminum alloys, including pure aluminum.

Besides anodizing the finishes produced in accordance with the present invention may be otherwise treated along conventional lines. In particular they form excellent bases for painting or lacquering and may be readily plated or otherwise chemically treated with excellent results.

Aluminum or its alloys treated in accordance with the above may be readily resistance welded without special cleaning.

Articles of aluminum or its alloys treated by our processes resist tarnish, corrosion and smudging to such extent that they may be placed on dealers' shelves without losing their appearance for very long periods; accordingly lac-

quering, generally required to keep such articles attractive for extended periods, is unnecessary.

Our processes may be used for chemically "machining" aluminum or its alloys to reduce or modify dimensions without the use of machinery. The chemical "machining" may be rendered selective by suitable masking. Deburring may be easily effected. In contrast with mechanical machining, no cold working occurs as is sometimes very objectionable.

What is claimed is:

1. The method of treating a surface of aluminum or an aluminum alloy comprising subjecting said surface to the action of an acidic mixture having a solvent action on said surface to produce a macroscopically uniform smooth finish, said mixture including as its essential constituents approximately 45% to 98% of free phosphoric acid, approximately 2% to 35% of water, and approximately ½% to 50% of free nitric acid, said action taking place at a temperature in the range from 150° F. to the boiling point of said mixture.

2. The method of treating a surface of aluminum or an aluminum alloy comprising subjecting said surface to the chemical, non-electrolytic action of an acidic mixture having a solvent action on said surface to produce a macroscopically uniform smooth finish, said mixture including as its essential constituents approximately 40% to 98% of free phosphoric acid, approximately 2% to 35% of water, and approximately ½% to 50% of free nitric acid, said action taking place at an elevated temperature in the range from 160° F. to the boiling point of said mixture, and subsequently oxidizing said surface.

3. The method of treating a surface of aluminum or an aluminum alloy comprising subjecting said surface to the chemical, non-electrolytic action of an acidic mixture having a solvent action on said surface to produce a macroscopically uniform smooth finish, said mixture including as its essential constituents approximately 45% to 98% of free phosphoric acid, approximately 2% to 35% of water, and approximately ½% to 50% of free nitric acid, said action taking place at an elevated temperature in the range from 160° F. to the boiling point of said mixture, and subsequently anodizing said surface.

4. The method of chemically brightening a surface of aluminum which comprises immersing said surface in an acidic mixture including, as its essential constituents, by weight, approximately 75 to 87.5% of free phosphoric acid and approximately 12.5 to 25% of water, with said mixture at a temperature in the range from approximately 160° F. to the boiling point thereof.

5. The method of chemically brightening a surface of aluminum which comprises immersing said surface in an acidic mixture including, as its essential constituents, by weight, approximately 65 to 85% of free phosphoric acid, approximately 5 to 34% of water, and approximately 1 to 10% of free nitric acid, with said mixture at a temperature in the range from approximately 160° F. to the boiling point thereof.

6. The method of chemically brightening a surface of aluminum which comprises immersing said surface in an acidic mixture including, as its essential constituents, by weight, approximately 45 to 98% of free phosphoric acid, approximately 2% to 35% of water, and approximately ½% to 50% of free nitric acid, with said mixture at a temperature in the range from approximately 160° F. to the boiling point thereof.

7. The method of producing a bright reflecting surface on aluminum articles which comprises immersing the aluminum article in a bath comprising as its essential constituents a major amount of phosphoric acid and a minor amount of nitric acid at a temperature of at least 200° F. for a period of time to subject the surface of the aluminum article to chemical action only of the bath to produce a polished, bright reflecting surface on said aluminum article.

8. The method of producing a bright reflecting surface on aluminum articles which comprises immersing the aluminum article in a bath comprising as its essential constituents 45 to 98% by weight of phosphoric acid and ½ to 50% by weight of nitric acid at a temperature of at least 200° F. for a period of time to subject the surface of the aluminum aritcle to chemical action only of the bath to produce a polished, bright reflecting surface on said aluminum article.

9. The method of chemically brighening a surface of aluminum which comprises immersing said surface in an acidic mixture including, as its essential constituents, phosphoric acid and water, the mixture containing, by weight, at least 65% of free phosphoric acid, with said mixture at a temperature in the range from 150° F. to the boiling point of said mixture.

10. A process for brightening metal from the group consisting of aluminum and alloys thereof which comprises immersing the metal in a bath having as the essential components thereof phosphoric acid of the formula H_3PO_4 and water, the phosphoric acid being present in an amount from about 65% to 98% by weight, and the bath being maintained at a temperature of at least 160° F.

11. The method of chemically brightening a surface of an aluminum article which comprises immersing said article in a solution having as the essential components thereof, on a weight basis referred to the total weight of phosphoric acid, nitric acid and water therein, about 45 to 98 per cent phosphoric acid, about ½ to 50 per cent nitric acid and about 2 to 35 per cent water, the solution being maintained at a temperature above about 160° F.

12. The method of chemically brightening a surface of an aluminum article which comprises immersing said article in a solution consisting of about 45 to 98 per cent phosphoric acid, about ½ to 50 per cent nitric acid and about 2 to 35 per cent water, on a weight basis, the solution being maintained at a temperature above about 160° F.

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