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3,575,747

CHEMICAL POLISHING OF ALUMINUM

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ABSTRACT OF THE DISCLOSURE

Strongly acidic compositions are provided for the bright polishing of aluminum, including its alloys. The compositions are characterized by the presence of nitric acid in amounts ranging from about 0.25% to about 10%, together with an effective nitrous acid content of 0.001% to 1%, or more. Phosphoric acid is used in substantial amounts in compositions giving highly specular finishes; though smoothing is achieved with phosphoric acid as low as 3%. Sulphuric acid is used when the phosphoric acid content is low. Most desirable compositions contain both phosphoric acid and sulphuric acid in total amounts in excess of 60%. The compositions are used at elevated temperatures.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is in part a continuation of Ser. No. 711,174, filed Mar. 7, 1968, now abandoned.

BACKGROUND OF THE INVENTION

The chemical polishing of aluminum is described in my Patent 2,729,551, dated Jan. 3, 1956, in which there is disclosed the use of polishing baths containing upwards of about 40% phosphoric acid and upwards of about 0.5% of nitric acid. In accordance with the patent, optimum specular effects are secured when the percentage of phosphoric acid is relatively high, for example in excess of 65%. For producing specular finishes, such baths are operated at relatively high temperatures ranging from about 180° F. to about 220° F. Times of immersion of the work could vary from a few seconds to around three minutes or more.

Baths of the type just mentioned have been modified in various ways, by additions of heavy metals such as copper and/or nickel, by the addition of non-aqueous diluents, such as aluminum salts, acetic acid, or the like, and by attempts to add sulphuric acid as a partial substitute for phosphoric acid. These modifications have met with varying degrees of success, but certain deficiencies have persisted which may be generally summarized as follows:

One of the most serious deficiencies of all of the heretofore known baths has been the limitation of permissible transfer time, i.e., the time permissible between withdrawal of aluminum articles from the polishing bath and immersion of the work in, or rinsing of the work by, water to stop reaction. As noted in my said patent, for the production of specular finishes the acid baths have had to operate at high temperatures. The baths capable of producing specular finishes at the high temperatures will actively produce etching of aluminum at lower temperatures. The action, both in polishing and etching, is one of aluminum solution. The limitation on transfer time may thus be readily understood:

When the work is withdrawn from the amply hot bath into the air its temperature rapidly drops into a range such as 150° F. to 180° F., within which the dissolving action

continues with rapid etching before the temperature drops to a point at which action terminates. In baths heretofore used, thirty seconds time of the work in the air has generally been the upper limit to avoid etching. In other words, no more than about thirty seconds was permissible as the time between withdrawal of the work from the polishing bath and quenching of the action in water. Considering that for practical purposes the aluminum articles must be supported by racks and handled by hoists, it will be evident that practical handling was difficult in the limited time permissible.

The necessary rapidity of the transfer had another disadvantage:

The baths, high in phosphoric content, were viscous, and drainage of bath liquid from the work took place relatively slowly, and drainage within the short permissible time was far from complete and relatively large quantities of the bath had to be carried over into the water, whereas, desirably, from the standpoint of effecting drainage the work should be held over the polishing bath to recover what was dragged out.

It was recognized that if at all possible sulphuric acid should be substituted to as great an extent as possible for the much more costly phosphoric acid. If sulphuric acid could be substituted, it was recognized that not only would the bath composition be cheaper but the viscosity of the composition would be lower leading to the possibility of a higher rate of drainage. Furthermore, baths containing a high percentage of phosphoric acid were relatively intolerant of accumulation of aluminum, which was dissolved in the polishing action, in that aluminum phosphate crystallized out even at elevated temperatures, and if the bath temperatures were permitted to drop, as when inactive at nights or over weekends, the baths would "freeze" by separation of aluminum salt. However, substantial amounts of sulphuric acid which might keep the aluminum better in solution, or increase of water content which would have the same results, were found to be inconsistent with production of highly specular results. To some extent sulphuric acid could be tolerated as the aluminum in solution rose in quantity; but this meant that a bath had to vary in composition during its useful life to maintain the achievement of satisfactory results.

A further disadvantage of the polishing baths was the evolution of nitrogen oxide fumes during operation. The existence of these fumes, highly poisonous in nature, necessitated ventilating systems which greatly interfered with work handling. To minimize these fumes proposals were made to incorporate into the bath ammonium salts or urea for chemical reaction with the nitrogen oxides.

SUMMARY OF THE INVENTION

In accordance with the present invention, polishing baths containing nitric acid are particularly characterized by containing also nitrous acid.

At this point it is appropriate to discuss what is meant by the presence of "nitrous acid" in the present disclosure. Chemical text books contain very confused statements regarding nitrous acid. It is recognized that it does not occur in a pure state. With reference to apparent solutions, statements are made, on the one hand, concerning its ready decomposition into nitrogen oxides, and on the other hand to reactions of nitrogen oxides with water to form nitrous acid. Nitrites in aqueous solution and in the cold appear to be decomposed by acids to form solutions which act as if they contain nitrous acid, though when nitrites are treated with strong acids vigorous reactions occur with evolution of nitrogen oxides.

For purposes of the present disclosure, relating to strongly acidic polishing baths, references will be made to the presence of nitrous acid, without regard to the

possible actualities of the situation, on the basis of its "apparent" presence in the baths to which the invention relates. This apparent presence of nitrous acid will be considered from the standpoint of the capability of diazotization of primary aromatic amines by diluted aqueous solutions of the baths. It has been found that baths effectively operable in accordance with the invention have the following characteristics:

If a sample of the bath is diluted with water and cooled and then added to a cooled acidic solution of a primary aromatic amine (such as aniline or paratoluidine), diazotization apparently occurs, and if a sample of the resulting solution is added to an alkaline solution of a phenol (such as phenol or betanaphthol) a characteristic azo dye is produced. Similar dye production occurs in the diazotizing reactions when a diluted bath is added to various amine mixtures as in the conventional colorimetric tests for nitrous acid. For purposes of the present invention, such production of an azo dye will be regarded as establishing the presence of nitrous acid in the polishing bath. When the presence of nitrous acid is referred to, it will be understood that this capability of producing an azo dye exists.

As will appear in greater detail hereafter, the presence of nitrous acid in a polishing bath may be achieved in several different ways:

First, a nitrite, such as sodium or potassium nitrite, or the nitrite of another acceptable metal, may be added, preferably in the cold, to one or more components of the final bath, or to the final bath itself. As will appear, the nitrous acid required is in small quantity, and the neutralization of the strong acids of the bath, present in considerable quantities, is essentially negligible. With careful addition of the nitrite, though some nitrogen oxides are generally evolved, the required nitrous acid remains in the bath and, in particular, at least to a major extent remains therein as the bath is heated to its operating temperature.

Secondly, the nitrous acid may be produced in the bath by reduction of excess nitric acid therein. This reduction may occur at room temperatures in the case of some reducing agents or only when the bath is heated toward or to operating temperatures in the case of other reducing agents. Nitrous acid is, in fact, preferably produced by such reduction which has the advantage of minimizing expense, a preferred reducing agent being inexpensive sodium sulfite. Referring to this last, the reaction producing the nitrous acid involves the reduction of nitric acid and the concurrent oxidation of sulphurous acid. The sulphite may be added to the cold composition containing nitric acid sufficiently slowly to avoid excessive loss of sulphur dioxide, and optimum results are secured if the sulphite is first dissolved in water to be added in making up the bath followed by the addition of nitric acid and then the addition of phosphoric and/or sulphuric acids. In providing nitrous acid in this fashion, account must be taken of the fact that the nitrous acid is produced at the expense of nitric acid, and since nitric acid is an essential constituent of a bath for effective brightening action, in ascertaining the proper amount of nitric acid to be used there must be taken into account that which will be lost (as nitric acid) by reduction to nitrous acid.

It is also possible to add nitrous acid directly by using fuming nitric acid which is, or at least may be regarded as, a solution of nitrous acid in nitric acid. To provide both acids, both ordinary nitric acid and an appropriate small amount of fuming nitric acid may be used; or if the nitric acid content is to be low, only fuming nitric acid may be used. A wide variety of fuming nitric acids are available; however, fuming nitric acid is not only unpleasant but dangerous to handle, and is not recommended for large scale use.

Still another mode of providing nitrous acid is to add compounds which effectively provide nitrous acid by decomposition; for example, nitrosylsulfuric acid (chamber crystals), may be added as a source of nitrous acid.

Particular compositions, and permissible ranges, will be hereafter described.

The presence of nitrous acid in the baths in accordance with the invention has a profound effect on their operation.

Particularly outstanding is the greatly increased permissible transfer time without etching. With the nitrous acid present it appears that when the temperature drops as the work is taken out of the hot polishing bath the action on the aluminum either substantially terminates or, if it continues, the action remains one of smoothing without producing the etching characterizing prior baths as their temperature was lowered. Accordingly, no haste is required and handling is simplified, while at the same time drainage of the carried out liquid is permitted to such extent as to minimize loss of the bath by dragout.

Secondly, the presence of the nitrous acid produces a high toleration of sulphuric acid in substitution for phosphoric acid. Specular finishes may be produced, for example, with as little as 7% of phosphoric acid in the bath. The advantages are obvious:

Inexpensive sulphuric acid can largely replace the much more costly phosphoric acid, and the viscosity of the bath is considerably lowered, promoting more complete drainage. Furthermore, a greater accumulation of aluminum in the baths is permissible without the disadvantage of crystallization of aluminum salts. It is also found that the percentage of water in the bath may be increased without deterioration of its results, and with still more increase in toleration of dissolved aluminum. Further, these results are all secured without increase in the amount of bath necessary to polish a given aluminum area.

A further, and surprising, result is that during the bath operation the evolution of nitrogen oxide fumes is greatly reduced. It could be expected, on the basis of text books, that possibly the nitrous acid would be decomposed with accelerated production of nitrogen oxide; but this is not the case.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The bath compositions provided in accordance with the invention comprise primarily phosphoric acid, sulphuric acid (if any), nitric acid and water. To such acid-water mixture there are added (from a final composition standpoint, and not necessarily in a particular sequence variously and in relatively small quantities the materials which are active in providing nitrous acid in accordance with the invention, and also additional materials, in some cases, which tend to promote brightness or smoothness, or which affect the reaction activity but seem to provide essentially non-aqueous diluents, or which have surface actions to provide smooth operation uniformly over the surfaces being treated, such as wetting agents and oily materials, the latter being of types described in my Patent 3,301,787, dated Jan. 31, 1967,

To present clear indications of the compositions involved, there will be adopted a form of presentation in which the acids and water are given in terms of percentages by weight adding up to 100% for the total of phosphoric acid plus sulphuric acid plus nitric acid plus water. Then there will be given (as small percentages) the amounts of the additional materials referred to 100% of the acid-water mixture. As will become evident hereafter, substantial variations in percentages of the major acids and water have little effect on the results except when these constituents approach bounding values; for example, when phosphoric acid content is quite low, 2 to 3%, a 1% difference becomes material, whereas, for instance, when the phosphoric acid content is around 20% changes of several percent have little effect on the results obtained. Similarly, when the nitric acid content is at a low value of about 0.2%, a change of 0.1% may be significant, though when the percentage is upwards of 0.5%, a few tenths of a percent is immaterial. Accordingly, the per-

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centages of phosphoric acid, sulphuric acid, nitric acid and water will be given in rounded figures.

Compositions provided in accordance with the invention will be discussed in a general sequence of range of phosphoric acid from high percentages to lower ones.

As an example of high phosphoric acid composition there may be cited one having the following percentages of the major acids:

	Percent
H ₃ PO ₄ -----	78.6
H ₂ SO ₄ -----	4.8
HNO ₃ -----	1.6
H ₂ O -----	15.0

To provide a bath there was added 1.3% of sodium sulphite (anhydrous). Operating at 190° F., bright specular finishes may be obtained with this composition with immersion times ranging from 1 minute to 3 minutes or upwards depending upon the initial condition of the aluminum surface. When the work is withdrawn from the bath into the air, no matter how long it remains there while undergoing draining and cooling, the brilliance of the surface is not affected by etching. In other words, the presence of nitrous acid due to reduction of nitric acid by the sodium sulphite apparently prevents completely what would ordinarily be an etching action as the temperature drops from the temperature of the bath to a value at which action essentially terminates.

It may be noted that if this composition is diluted by adding as much as 10% of water to the original mixture best results are obtained by raising the bath temperature to 210° F. But the remaining results are the same.

The foregoing example illustrates the matter of prevention of etching during transfer. However, the composition is not of a preferred type because it does not take advantage of the substitution of sulphuric acid for phosphoric acid as already discussed, the composition being viscous, so that draining is prolonged, and being relatively expensive.

As a further example of a high phosphoric acid composition, there may be cited one which contains acids and water as follows:

	Percent
H ₃ PO ₄ -----	71.8
H ₂ SO ₄ -----	4.5
HNO ₃ -----	2.2
H ₂ O -----	21.5

To this acid mixture was added 2.5% of alumina which dissolved in the acid mixture. Also added was 0.25% of sodium nitrite. This composition gave best results around 210° F. with the same conditions of operation (immersion 2 minutes) and results as described in connection with the previous example. (Immersion times will be understood to be, in the following examples, 1 to 3 minutes, the time being non-critical.)

With an increase of the sodium nitrite to 2% or more, the optimum temperature of operation rises to 230° F.

(It may be here noted that the percentages of the acids are not shown as reduced in the assumed formulation because of partial use in solution of the alumina or in their use in decomposing sodium sulphite or sodium nitrite, actual neutralization being negligibly small. Nor is the percentage of nitric acid considered as reduced by the reducing agent such as sodium sulphite. As will be particularly pointed out later, when a reducing agent is used the desirable amount of nitric acid should be correspondingly increased since unreduced nitric acid is essential for proper results.)

While sulphuric acid has been indicated as used in small amount in the foregoing compositions, it need not be present at all, the compositions, from the standpoint of major acid content, being similar to those heretofore

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used in the art not involving sulphuric acid. As an example there is the following composition:

	Percent
H ₃ PO ₄ -----	61.3
HNO ₃ -----	2.9
H ₂ O -----	35.8

To this was added to provide the final composition 1.2% of sodium nitrite, the composition being used at 230° F. to provide results similar to those already discussed. It will be noted that the water content in this composition is quite high. This composition, without nitrous acid, would not be satisfactory, producing an etch. This illustrates the advantage of nitrous acid in increasing tolerance of water.

References may now be made to a number of compositions which fall in a preferred range for several reasons:

Not only do they prevent transfer etch and reduce evolution of nitrogen oxide gases, but they contain large quantities of sulphuric acid with its advantage of relative cheapness and reduction of bath viscosity to promote drainage and thus reduce dragout losses. Furthermore, these compositions are suitable for producing specular finishes on a wide variety of aluminum alloys, whereas some of the compositions, like those previously discussed, will produce specular finishes only on selected alloys. The susceptibilities of aluminum alloys to bright chemical polishing are well known and need not be discussed in detail. In practice, of course, when bright polishing is to be effected choices of alloys are made on the basis of suitability for the mechanical and visual needs (color) and the degree of polishing required.

One of the preferred compositions is as follows:

	Percent
H ₃ PO ₄ -----	55.0
H ₂ SO ₄ -----	28.0
HNO ₃ -----	4.5
H ₂ O -----	12.5

to which is added 4% of alumina and 0.05% of crystalline nickel nitrate, with addition of 0.5% of sodium nitrite to provide the desired properties in accordance with the invention. This composition gives best results at about 215° F.

Another composition comprises:

	Percent
H ₃ PO ₄ -----	53.8
H ₂ SO ₄ -----	33.5
HNO ₃ -----	1.6
H ₂ O -----	11.1

To the foregoing there is added 0.05% of nickel nitrate and 0.2% of anhydrous sodium sulphite. This bath was found to give best results at 170° F.

One of the best baths found for consistent operation giving rise to all of the advantages of the invention and particularly useful in the brightening of an extremely large variety of aluminum alloys is one comprising:

	Percent
H ₃ PO ₄ -----	49.8
H ₂ SO ₄ -----	32.2
HNO ₃ -----	4.8
H ₂ O -----	13.2

To this composition is added 0.05% of nickel nitrate, 5% of alumina and 0.4% of anhydrous sodium sulphite. This bath may be used at various temperatures depending upon the alloys treated, the optimum temperatures being in a range of around 200 to 210° F.

A further composition still in the preferred range:

	Percent
H ₃ PO ₄ -----	40.2
H ₂ SO ₄ -----	44.2
HNO ₃ -----	4.7
H ₂ O -----	10.9

To this is added to form the bath 3% of alumina, 0.05% of nickel nitrate and 0.2% of anhydrous sodium sulphite. Optimum operation for most polishable alloys is at 210° F.

A composition still lower in phosphoric acid but giving excellent results is the following:

	Percent
H ₃ PO ₄ -----	26.3
H ₂ SO ₄ -----	65.5
HNO ₃ -----	1.1
H ₂ O -----	7.1

to which is added 0.04% of crystalline nickel nitrate, 0.02% of crystalline copper nitrate and 0.8% of anhydrous sodium sulphite. Operation is desirably at about 210° F.

Variants of the foregoing composition are illustrative of the ranges of components. The sodium sulphite addition may range up to 2.0% or more, though in the higher portions of this range additional nitric acid is desirable to maintain a nitric acid content despite reduction by the sulphite. On the other hand, the nitric acid may be present in about half the amount indicated, i.e. 0.5%, with a slight drop in specularity, but in that case the sulphite addition should be in the lower portion of the range, i.e. around 0.3%.

The following bath has a quite low phosphoric acid content:

	Percent
H ₃ PO ₄ -----	11.6
H ₂ SO ₄ -----	59.4
HNO ₃ -----	4.4
H ₂ O -----	24.6

To this is added to provide nitrous acid 0.2% of sodium nitrite. Optimum operation of this bath is at relatively low temperatures ranging from 140° F. to 180° F.

Fair specular finishes are provided by the following composition operated at around 230° F.:

	Percent
H ₃ PO ₄ -----	8.6
H ₂ SO ₄ -----	85.2
HNO ₃ -----	1.4
H ₂ O -----	4.8

To the foregoing is added 1.5% of sodium nitrate.

A rather similar composition but with considerably lower nitric acid is the following:

	Percent
H ₃ PO ₄ -----	8.8
H ₂ SO ₄ -----	86.6
HNO ₃ -----	0.25
H ₂ O -----	4.35

To the foregoing is added 0.3% of anhydrous sodium sulphite. Here again optimum operation is at 230° F. to provide specular finishes.

A smooth but lower grade specular finish may be obtained with even lower phosphoric acid content using the following composition at a relatively low temperature of 180° F.:

	Percent
H ₃ PO ₄ -----	5.4
H ₂ SO ₄ -----	67.0
HNO ₃ -----	4.1
H ₂ O -----	23.5

To this bath is desirably added about 8% of alumina and 0.8% of sodium nitrite.

A composition very low in phosphoric acid is the following:

	Percent
H ₃ PO ₄ -----	2.7
H ₂ SO ₄ -----	88.2
HNO ₃ -----	0.6
H ₂ O -----	8.5

To the foregoing was added 0.1% of crystalline nickel nitrate and 2.5% of alumina, nitrous acid being provided

by the addition of 1.5% of sodium nitrite. The foregoing composition used at 220° F. produced smooth brightening of aluminum though the finish was not specular.

In summary of the foregoing, and as a result of numerous further tests, it has been found that the treating solutions for highly satisfactory results, in preventing transfer etch, securing effective brightening action, and prevention of noxious fumes, should contain a minimum of about 0.001% of nitrous acid. Nitrous acid may be present in such low quantities particularly when the baths contain relatively large quantities of non-aqueous diluents such as aluminum salts and/or when they contain copper and/or nickel in solution, the percentage being based, as before, on 100% of the acid-water mixture. The nitrous acid is provided by the addition of a soluble nitrite, by the addition of a sulphite, or by the addition of other anionic nitric acid reducing agents as set forth more fully hereinafter. The maximum concentration of nitrous acid is not critical, though additions in excess of about 1.5% are merely wasteful of materials and with too much nitrous acid there reappears evolution of nitrogen oxides. The amount of nitrous acid present may be determined by permanganate titration in usual fashion, or by iodide titration (also conventional), or by the known colorimetric methods using azo dye formation, as the well known method using sulphanilic acid and alphanaphthylamine.

While, as stated, nitrous acid is effective in concentrations as low as 0.001% in the presence of other materials, e.g., alumina, such a low percentage is quickly exhausted by treatment of small amounts of aluminum, and for commercial purposes a minimum of about 0.01% should be used, since then the bath remains effective to the point when replenishment is required by reduction of volume and change of composition as discussed more fully hereafter. When replenishment occurs the bath is restored to a content of 0.01% or more of nitrous acid and it then may ordinarily be continued in operation indefinitely. Most practical are baths containing nitrous acid in amounts produced by addition of 0.2% to 1.3% or more of sodium sulphite or 0.2% to 1.5% or more of sodium nitrite, as exemplified by the examples given above.

The phosphoric acid may range, based on 100% for the acid-water mixture from around 3% minimum to 80% or more, and in fact with high sulphuric acid content fair results are secured with even less than 3% of phosphoric acid. The sulphuric acid may be absent; but to secure all of the advantages of the invention it is desirably present, and in amounts such that the total content of phosphoric acid and sulphuric acid is at least 60%. Most desirably the sum of percentages of these two acids is upwardly of 70%, while when the phosphoric acid is quite low (3% to 8%) it is most desirable to have the sum of these two acids around 90% or more. The total of these two acids may be 95% or more, as indicated by the example in which the total is 95.4%, using 8.8% of phosphoric acid. It is when the sulphuric acid content is high that the effect of nitrous acid in producing specularity is most significant; baths so high in sulphuric acid that they would produce etching in the absence of nitrous acid will not produce etching when nitrous acid is present even in quite small amounts, e.g. 0.01%. The other effect of the presence of nitrous acid, avoidance of etching during transfer, occurs whether or not the bath without nitrous acid will produce brightening.

The content of nitric acid follows, generally, the practices heretofore involved in this art. As little as 0.25% may be used, but for best brightening results a practical minimum is about 1.0%. 5% is generally a practical upper limit because larger amounts are essentially wasteful, and nitrogen oxides are evolved, there being produced no better results from the standpoint of brightening. Recommended generally for practical use are amounts ranging between 1.0% and 3.0%. Since 10% of nitric

acid may be used, when inhibitors such as aluminum salts are present in large amounts, without passing into the realm of highly objectionable fuming, this percentage is herein adopted as an upper limit. With more than 10% nitric acid the nitrous acid is ineffective to produce its stated desirable results.

In the foregoing, primary reference has been made to the use of sodium sulphite to provide nitrous acid in baths by reduction of nitric acid, since sodium sulphite is inexpensive and thoroughly effective. However, it is merely one of a broad class of compounds which may be used to reduce nitric acid for the purposes of this invention. Numerous normal sulphites may, of course, be used, and bisulphites, preferably of alkali metals, may equally be used. Thiosulphates, phosphites and similar inorganic reducing agents, having oxidizable anion groups, may also be used. Equally usable are many organic materials which are capable of reducing nitric acid with the formation of nitrous acid. Some of these perform the reduction at ordinary temperatures. Others when added to a bath in the cold will not immediately produce the reduction or will do so only to a limited extent; but when the baths are heated to their operating temperatures, such materials will provide more complete reduction with the end result that the proper quantity of nitrous acid is in the bath. Among the many materials which provide reduction there may be cited formic acid (which may be added as an alkali formate), lower alcohols, and the like. Sugars are examples of organic reducing agents which may not produce full reduction at ordinary temperatures but which do so when the temperatures of the baths rise to operating conditions, though only small amounts may be used. In some cases the reducing reactions may be accompanied by other reactions. For example phenol added to the bath apparently undergoes nitration, but in the process of this nitration nitrous acid is also produced.

The amounts of organic materials which are added may be readily ascertained by tests to provide nitrous acid content of a bath which conforms to the minimum or more as set forth above; the extent of reduction is generally unpredictable ab initio because the action of nitric acid on organic compounds is generally complex in that, for example, even alcohols are not oxidized by nitric acid completely to carbon dioxide and water.

What is required in the way of nitric acid reduction is that nitrous acid should be produced in sufficient quantity and should be evidenced by its apparent existence demonstrated by the capability of effecting diazotization as described above. Some materials which are ordinarily regarded as reducing agents and which, under other conditions, are attacked by nitric acid do not produce nitrous acid in the sense herein indicated; for example, ethylene glycol is relatively ineffective in producing nitrous acid through small amounts are detectable by applying the diazotization test. On the other hand, hexylene glycol is effective in producing nitrous acid when used in small quantities.

It may be here remarked that the presence of substances incompatible with or forming compounds with nitrous acid should not be used. Ammonium salts, for example, will destroy nitrous acid, probably forming ammonium nitrite (in the ionic sense) initially in the cold which at bath operating temperatures will break down to form nitrogen. Amines and amides are other classes of incompatible materials, as are also iron salts.

Certain ranges of bath compositions stand out as particularly useful in securing bright specular finishes. For example, in the case of low sulphuric acid compositions the bath may comprise approximately 60% to 92% of phosphoric acid, 0 to 2% of sulphuric acid, 1% to 10% of nitric acid, and 7% to 35% of water, with the total of phosphoric acid and sulphuric acid amounting to approximately 60% to 92%, with nitrous acid present, as before, in amounts ranging from approximately 0.01% to 1.5% for practical compositions. Such baths may also contain

copper, nickel and/or alumina, or other additives, as already discussed, these being particularly required when the nitric acid content is high.

Another range of preferred compositions are baths containing approximately 7% to 80% of phosphoric acid, 0 to 85% of sulphuric acid, approximately 1% to 10% of nitric acid, and 7% to 17% of water, with the total of phosphoric acid and sulphuric acid amounting to approximately 73% to 92%, with nitrous acid, as before, present in amounts ranging from approximately 0.01% to 1.5%.

Still another range of bath compositions giving advantageous results comprise approximately 20% to 80% of phosphoric acid, approximately 0 to 72% of sulphuric acid, approximately 1% to 10% of nitric acid and approximately 7% to 32% of water, with the total of phosphoric acid and sulphuric acid approximately in the range of 60% to 92%, with nitrous acid present in amounts ranging from approximately 0.01% to 1.5%.

All of these compositions may have additives of the types previously mentioned.

The maintenance of the polishing baths is effected by adding replenish solutions which are related to the original bath composition. As will be evident from the foregoing, the ranges of operation are broad so that it is by no means necessary to maintain during operation bath compositions which are very closely related to the original compositions. For example, a bath composition in the preferred range may very well have its composition changed, particularly with respect to phosphoric acid and sulphuric acid, by percentages of these constituents ranging through plus or minus 10%. However, the following are the general rules relating to addition of replenishing compositions:

First, it is good practice to add replenishing composition when the volume of the bath decreases by not less than about 3% and by not more than about 7%. Replenishment if the volume decreases by less than 3% represents merely a wasteful operation. When the volume decreases by more than about 7% the bath is likely to have become unbalanced.

The requirements for replenishment arise primarily because of losses of nitric acid, nitrous acid, and water at a greater rate (change of original percentage) than phosphoric and sulphuric acids. The latter are lost primarily through dragout. This dragout has one advantageous result in that by reason of it the accumulation of the aluminum is kept within proper bounds. But by reason of chemical reaction nitric acid is lost and by reason of the operation of the baths at elevated temperatures both water and nitric acid are lost. The replenishing compositions are, accordingly, richer in nitric acid and water than the bath composition.

In general, considering a particular initial bath, nitric acid in the replenishing composition should be from 2.75 to 3.75 times the percentages in the original composition.

The replenish composition should have from two times to three times the water of the original bath composition, the former factor applying when the water in the composition of the original bath is high, ranging to the higher factor when the water content of the original bath is low.

The remainder of the composition, besides that portion representing nitrous acid, will largely be phosphoric acid and sulphuric acid (if the latter is used) and the ratio of these acids should be generally similar to the ratio in the original bath, though the ratio may vary considerably as will have already been evident from the examples given.

As a result of these considerations, replenishing compositions may contain a minimum of about 1.3% and a maximum of 15%, or even more, of nitric acid. The water in the replenishing solution may be up to as much as 80%, while the minimum amount of water will be in the neighborhood of about 12%.

In considering optimum replenishing operations, specif-

ic gravity may be used as a criterion. After adjustment of the ratio of phosphoric and sulphuric acids, and the provision of the amount of nitric acid in accordance with the foregoing, it has been found advantageous to adjust, by addition of water, the specific gravity of the replenishing composition to a value of 0.23 to 0.28 less than the specific gravity of the fresh bath. For example, if the fresh bath has a specific gravity of 1.73, a satisfactory replenishment composition would be adjusted by water addition to a specific gravity of 1.50 to 1.45.

It will be noted that with addition of replenishment solution under proper conditions there will be no violent change in the bath composition since the volume will ordinarily have been reduced by only 3% to 7%. Thus, even though the nitric acid content of the replenishing solution is high, the nitric acid content of the bath remains low.

In accordance with the present invention the nitrous acid content of the bath must also be maintained, and desirably the replenish composition will contain substantially the same percentage of the nitrous acid providing material as the original bath: i.e., equivalent to at least 0.01% of nitrous acid.

For example, consider one of the best original bath compositions found and containing:

	Percent
H ₃ PO ₄ -----	53.6
H ₂ SO ₄ -----	28.4
HNO ₃ -----	4.4
H ₂ O -----	13.6

to which was added 4% of alumina, 0.045% of crystalline nickel nitrate, and 0.33% of anhydrous sodium sulphite.

A suitable replenish solution for the foregoing contains approximately:

	Percent
H ₃ PO ₄ -----	35.4
H ₂ SO ₄ -----	18.8
HNO ₃ -----	13.5
H ₂ O -----	32.3

added to which is nickel nitrate 0.05% and sodium sulphite 0.4%. It will be noted that in this case the ratio of phosphoric acid to sulphuric acid is approximately maintained while the nitric acid is increased by a factor of approximately 3 and the water is increased by a factor of approximately 2.4. The sodium sulphite addition is about the same as that added to the original bath and is sufficient to maintain the advantages of the presence of nitric acid.

Already indicated in connection with the particular examples is the fact that the various compositions may produce either highly specular finishes or finishes which approach specular. The temperature ranges which have been given have been specified with particular reference to the brighter or more specular results. However, some commercial requirements relate to the obtaining of smooth surfaces short of being what might be regarded as specular, these requirements relating, for example, to the avoidance of glare in automotive uses or the like. Such desired finishes, with achievement of the other advantages of the invention may be produced by such variations as the use of less nitric acid or the use of more water, or by merely effecting the brightening action at lower temperatures. The presence of nitrous acid in accordance with the invention prevents transfer etch and promotes uniform brightening as compared with non-uniform brightening. The smoothing in such cases may actually result in less brightness than the aluminum before treatment.

For the numerous specific compositions given above particular optimum temperatures or ranges of temperatures have been specified. For the preferred compositions the optimum temperatures generally fall in the range of about 200° F. to 215° F. It is quite impossible to give

for an arbitrary composition falling within the invention what the optimum temperature range for operation may be except by comparison with the examples. But several considerations provide guides for estimation of the temperature range to choose.

As is general with chemical reactions, temperature rise increases activity. Activity in the present treatments may be considered as measured by the rate of solution of aluminum. This activity is dependent on the ingredients and their proportions in the composition. Increase in inactive constituents such as aluminum salts, alkali metal salts, also acetic acid, decreases the activity in the bath and, to some extent, during transfer time; and this is also the effect of increase in content of nitrous acid in accordance with the invention. Increase of sulfuric acid, when the phosphoric acid is very low, and increase of water increases activity. Excessive addition of nitric acid also increases activity; though increase of content of nitric acid in the low range thereof decreases activity. Highest specularly requires restriction of activity and the assumption may be made that if a known composition (such as that of one of the examples given) is changed in the direction of higher activity the temperature should be lowered, and vice versa, for the treatment of the same alloy. But the activity depends also on the alloy being treated, so that simple tests are generally desirable to ascertain, for a chosen composition, for the alloy to be treated, and especially for the results desired (high specularly, brightening, smoothing, color, etc.), the best temperature to use. It may be noted that when the conditions are such that optimum results are secured at a low temperature with a highly active bath, too great an increase in temperature may cause the bath to become so active that its activity cannot be sufficiently inhibited by the presence of nitrous acid; for example, a bath having optimum activity at 170° F. to 190° F. cannot be expected to be used at 210° F. without etching both during the treatment in the bath and during transfer. Statements of temperature ranges for the practice of the invention are not to be taken as meaning that all compositions within the scope of the invention may be used at any arbitrary temperature within the range.

To summarize, the invention includes the following:

First, baths for the chemical polishing of aluminum and alloys thereof (i.e., alloys primarily of aluminum and containing conventional alloying materials) in accordance with the invention, each of which baths comprises, as its major constituents, a mixture of approximately 3% to 80% of phosphoric acid, sulphuric acid 0% upwards and such that the total of phosphoric acid and sulphuric acid, if any, is in the range of approximately 60% to 95%, approximately 0.25% to 10% (but preferably less) of nitric acid, and approximately 5% to 40% of water, and, on the basis of consideration of the foregoing acids and water as 100%, approximately 0.01% to 1.5% of nitrous acid.

Secondly, methods involving immersion of aluminum articles in the foregoing baths, with the baths operating at temperatures in the range of 140° F. to the boiling point thereof. The temperature of 140° F. is approximately the minimum for effective brightening action of these baths, although some brightening or smoothing occurs with minimal activity on the aluminum surfaces even at ambient temperatures.

Third, the invention comprises replenishing compositions for the foregoing baths, which replenishing compositions comprise, as their major constituents, approximately 1.3% to 15% of nitric acid, approximately 12% to 80% of water, approximately 0.01% to 1.5% of nitrous acid, and as their other major constituent phosphoric acid or a mixture of phosphoric and sulphuric acids.

Fourth, the invention includes the method of replenishing baths of the type first mentioned using the last-mentioned replenishing compositions, the replenishment involving the addition of the replenishing composition to a bath when the volume of the bath is reduced, by its use,

by approximately 3% to 7% of its original volume, the replenish composition being added in an amount to restore approximately the original volume of the bath.

It will accordingly be understood that the invention is not to be regarded as limited except as required by the following claims.

I claim:

1. A bath for the chemical polishing of aluminum and alloys thereof comprising, as its major constituents, a mixture of approximately 3% to 80% of phosphoric acid, sulphuric acid 0% upwards and such that the total of phosphoric acid and sulphuric acid, if any, is in the range of approximately 60% to 95%, approximately 0.25% to 10% of nitric acid, and approximately 5% to 40% of water, and, on the basis of consideration of the foregoing acids and water as 100%, approximately 0.01% to 1.5% of nitrous acid, all percentages being by weight.

2. A bath for the chemical polishing of aluminum and alloys thereof comprising, as its major constituents, a mixture of approximately 60% to 92% of phosphoric acid, sulphuric acid 0% to 2% and such that the total of phosphoric acid and sulphuric acid, if any, is in the range of approximately 60% to 92%, approximately 1% to 10% of nitric acid, and approximately 7% to 35% of water, and, on the basis of consideration of the foregoing acids and water as 100%, approximately 0.01% to 1.5% of nitrous acid, all percentages being by weight.

3. A bath for the chemical polishing of aluminum and alloys thereof comprising, as its major constituents, a mixture of approximately 7% to 80% of phosphoric acid, sulphuric acid 0% to 85% and such that the total of phosphoric acid and sulphuric acid, if any, is in the range of approximately 73% to 92%, approximately 1% to 10% of nitric acid, and approximately 7% to 17% of water, and, on the basis of consideration of the foregoing acids and water as 100%, approximately 0.01% to 1.5% of nitrous acid, all percentages being by weight.

4. A bath for the chemical polishing of aluminum and alloys thereof comprising, as its major constituents, a mixture of approximately 20% to 80% of phosphoric acid, sulphuric acid 0% to 72% and such that the total of phosphoric acid and sulphuric acid, if any, is in the range of approximately 60% to 92%, approximately 1% to 10% of nitric acid, and approximately 7% to 32% of water, and, on the basis of consideration of the foregoing acids and water as 100%, approximately 0.01% to 1.5% of nitrous acid, all percentages being by weight.

5. The method for the chemical polishing of aluminum and alloys thereof comprising their immersion in a bath having a temperature in the range of 140° F. to the boiling point of the bath, the bath comprising, as its major constituents, a mixture of approximately 3% to 80% of phosphoric acid, sulphuric acid 0% upwards and such

that the total of phosphoric acid and sulphuric acid, if any, is in the range of approximately 60% to 95%, approximately 0.25% to 10% of nitric acid, and approximately 5% to 40% of water, and, on the basis of consideration of the foregoing acids and water as 100%, approximately 0.01% to 1.5% of nitrous acid, all percentages being by weight.

6. A replenishing composition for a bath for the chemical polishing of aluminum and alloys thereof, which bath comprises, as its major constituents, a mixture of approximately 3% to 80% of phosphoric acid, sulphuric acid 0% upwards and such that the total of phosphoric acid and sulphuric acid, if any, is in the range of approximately 60% to 95%, approximately 0.25% to 10% of nitric acid, and approximately 5% to 40% of water, and, on the basis of consideration of the foregoing acids and water as 100%, approximately 0.01% to 1.5% of nitrous acid, said replenishing composition comprising, as its major constituents, approximately 1.3% to 15% of nitric acid, approximately 12% to 80% of water, approximately 0.01% to 1.5% of nitrous acid, and as its other major constituent phosphoric acid or a mixture of phosphoric acid and sulphuric acids, all percentages being by weight.

7. The method of replenishing a bath for the chemical polishing of aluminum and alloys thereof, which bath comprises, as its major constituents, a mixture of approximately 3% to 80% of phosphoric acid, sulphuric acid 0% upwards and such that the total of phosphoric acid and sulphuric acid, if any, is in the range of approximately 60% to 95%, approximately 0.25% to 10% of nitric acid, and approximately 5% to 40% of water, and, on the basis of consideration of the foregoing acids and water as 100%, approximately 0.01% to 1.5% of nitrous acid, the method comprising adding to the bath, when its volume is reduced, by use, by approximately 3% to 7% of its original volume, a replenish composition to restore approximately its original volume, the replenish composition comprising, as its major constituents, approximately 1.3% to 15% of nitric acid, approximately 12% to 80% of water, approximately 0.01% to 1.5% of nitrous acid, and as its other major constituent phosphoric acid or a mixture of phosphoric acid and sulphuric acids, all percentages being by weight.

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JACOB H. STEINBERG, Primary Examiner

U.S. Cl. X.R.

156—21; 252—79.2

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,575,747

Dated April 20, 1971

Inventor(s) Charles C. Cohn

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 14, line 30, after "nitric" insert -- acid, and approximately 5% to 40% of water, and, on the --.

Signed and sealed this 14th day of March 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents