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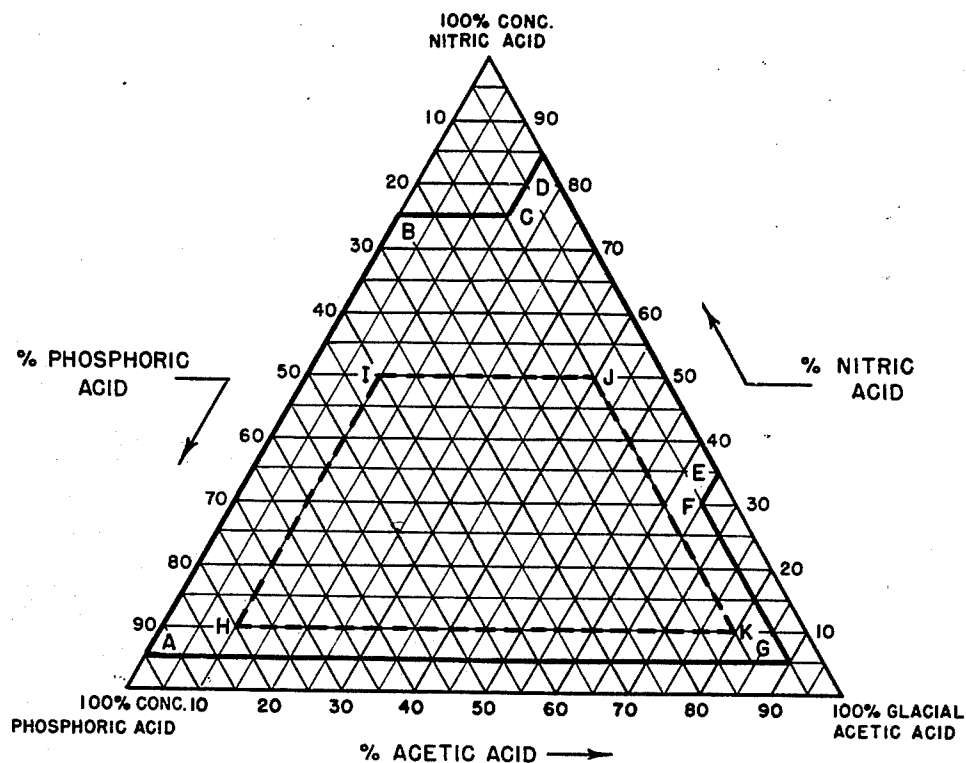
H. A. H. PRAY ET AL

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CHEMICAL POLISHING OF METAL SURFACES

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FIGURE 1



INVENTORS

Henry A. Holden Pray
Iver Igelsrud
Gerald L. Simard

BY *R. R. Adams*
AGENT

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CHEMICAL POLISHING OF METAL SURFACES

Henry A. Holden Pray and Iver Igelsrud, Columbus, Ohio, and Gerald L. Simard, Stamford, Conn., assignors, by mesne assignments, to The Battelle Development Corporation, Columbus, Ohio, a corporation of Delaware

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This invention relates to the polishing of metal surfaces. More particularly it relates to a method and a composition for the polishing of such surfaces by chemical means, and it is primarily concerned with chemical treatments to polish the surfaces of metals and alloys such as "German silver," copper, brass, nickel, and "Monel."

It has been common practice for many years to remove oxide scale from metallic surfaces by various pickling treatments, and numerous types of pickling baths have been developed. The object of such treatments is to remove the scale without, or with minimum, attack of the metal surface. More recently, a slightly different field of chemical treatment has been developed in which the metal surface is attacked by the treating solution and brightened to a considerable degree. This latter treatment, usually termed "bright dipping," has been applied to numerous metals and alloys such as copper and its alloys, aluminum and its alloys, magnesium and its alloys, silver and its alloys, zinc, cadmium, and stainless steels.

In general, the baths most commonly used in the prior art for bright dipping have been composed primarily of sulfuric acid, nitric acid, or of mixtures of sulfuric and nitric acids. Minor additions of many other materials, such as other acids, metallic salts, organic compounds, carbonaceous materials, etc., have been suggested to aid in controlling the character of the brightening action of these baths.

For example, a recommended bright dipping procedure for German silver is as follows: First, treat the scale-free surface in a prepickling bath composed of 10 liters of concentrated nitric acid, 50 grams of sodium chloride, and 0.2 liter of a solution of soot in nitric acid; rinse; and treat in a final brightening bath composed of 3 liters of concentrated nitric acid, 5 liters of concentrated sulfuric acid, 40 grams sodium chloride, and 0.2 liter of a solution of soot in nitric acid.

A commonly used bright dip for copper and its alloys consists of 2 gallons of concentrated sulfuric acid, 1 gallon of concentrated nitric acid, $\frac{1}{4}$ to $\frac{1}{2}$ ounce of sodium chloride, and 1 quart of water.

For nickel, the following procedure has been recommended: Dip for from 5 to 30 seconds in a bath composed of 1,000 cubic centimeters of water, 1,500 cubic centimeters of concentrated sulfuric acid, 2,250 cubic centimeters of concentrated nitric acid, and 30 grams of sodium chlo-

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ride; rinse; and neutralize in 1 percent ammonia solution.

The following brightening treatment has been suggested for use in connection with Monel: Dip in a bath composed of 1,000 cubic centimeters of water, 1,000 cubic centimeters of concentrated nitric acid, and 60 to 90 grams of sodium chloride; rinse in hot water; dip for less than 5 seconds in a bath composed of 1,000 cubic centimeters of water and 1,000 cubic centimeters of concentrated nitric acid; rinse; and neutralize in a 1 percent ammonia solution.

A recommended bright dip for stainless steel comprises a solution containing 25 per cent of concentrated hydrochloric acid, 5 per cent of concentrated nitric acid, and 0.5 per cent of a restrainer such as "Rodine," all percentages by volume. This bath is preferably used at approximately 150° F.

There are, however, certain undesirable features in the use of sulfuric and nitric acids, either individually or as a combination of the two, as bright dipping baths. In general, either such baths tend to be extremely reactive, in which case the work must be removed quickly after insertion with resulting lack of control and high drag-out losses, or they tend to be relatively inactive, in which case excessively long treatment times are required. Although the rapid reaction rates of some of the bright dips can be decreased considerably by the addition of oxidizing acids such as chromic, such additions are not completely effective in solving the problem because, in these baths, they tend to decrease the uniformity of the etch. Furthermore, nitric acid alone or mixtures of sulfuric and nitric acids tend, during use as bright dips, to give off fumes of nitrogen dioxide. These fumes are not only particularly corrosive, but they also have a marked physiological effect and constitute an industrial hazard. Chromic acid additions have been found to be at least partially effective in reducing this tendency. In addition, these prior art baths have a further drawback in that they require extremely careful cleaning of the surface to be brightened to remove all traces of grease or oil films or the resulting action will not be uniform.

The above-mentioned bright dips apparently produce their brightening action by chemically removing the last traces of the oxide scale and producing a contrast etch. This contrast etch results from the attack of certain faces of the metallic crystals, thereby producing facets which act as minute reflecting surfaces and create the

Cu alloy

precleaning

brilliant appearance. Because of this etching action, however, the articles so treated, even though brilliant, are not highly reflective or mirror-like.

A still more recent development in the treatment of metal surfaces is the discovery of anodic polishing. By this process, usually called electropolishing, which involves making the surface to be polished the anode in an acid electrolyte, a smooth, plane surface is obtained. This surface is not only brilliant, as is the surface obtained by certain bright dips, but it is also unetched and, therefore, has the highly reflective qualities of a mirror.

It is therefore one object of this invention to develop a chemical treatment for metal surfaces capable of producing a brilliant, smooth, highly reflective, unetched, polished surface.

Another object of our invention is to develop a chemical polishing bath for the treatment of metal surfaces which has an intermediate reaction speed, thereby making possible the proper control of the treating operation and permitting the polished articles to be drained for a sufficient length of time to prevent excessive bath losses from drag-out without requiring the use of excessive and uneconomically long treating times.

A further object of our invention is to develop a bath for chemically polishing metal surfaces which does not give off appreciable quantities of corrosive or noxious gases.

Another object of our invention is to develop a bath for the chemical polishing of metal surfaces that has a solvent action for grease and oil and, therefore, does not require that all traces of grease and oil films be removed from the metal surface prior to treatment.

Yet another object of our invention is to provide a bath for the polishing of metal surfaces that is not extremely critical in regard to composition or to temperature of operation.

Still a further object of our invention is to develop a bath for the production of smooth, brilliant polishes on metal surfaces which has a uniform action over large areas and which does not etch the surface even though the action is allowed to continue longer than is necessary for the production of a polish.

Other and further objects will be apparent from the following description and appended claims.

In contrast to the bright etches resulting from the use of nitric acid or of mixtures of nitric and sulfuric acids, we have found that mixtures of nitric acid plus acetic acid and phosphoric acid, either singly or preferably in combination, are capable of producing lustrous, highly reflective, mirror-like surfaces on "German silver," copper, brass, nickel, and "Monel." Our invention, in its preferred form, is illustrated in the drawing and is hereinafter fully described.

In the drawing, the figure represents a triaxial diagram showing the relative proportions of nitric acid, acetic acid, and phosphoric acid applicable for use in the polishing baths coming within the scope of this invention.

In the diagram, the respective sides of the triangle indicate the volume percentages of concentrated nitric acid, glacial acetic acid, and concentrated phosphoric acid, from 0 to 100 per cent.

The bath compositions that are operative for the chemical polishing of the above-noted metals and alloys are approximately defined on the accompanying triaxial diagram by the solid lines AB, BC, CD, DE, EF, FG, and GA, the approxi-

mate coordinates of the points being: A—5 per cent concentrated nitric acid, 0 per cent glacial acetic acid, and 95 per cent concentrated phosphoric acid; B—75 per cent concentrated nitric acid, 0 per cent glacial acetic acid, and 25 per cent concentrated phosphoric acid; C—75 per cent concentrated nitric acid, 15 per cent glacial acetic acid, and 10 per cent concentrated phosphoric acid; D—85 per cent concentrated nitric acid, 15 per cent glacial acetic acid, and 0 per cent concentrated phosphoric acid; E—35 per cent concentrated nitric acid, 65 per cent glacial acetic acid, and 0 per cent concentrated phosphoric acid; F—30 per cent concentrated nitric acid, 65 per cent glacial acetic acid, and 5 per cent concentrated phosphoric acid; and G—5 per cent concentrated nitric acid, 90 per cent glacial acetic acid, and 5 per cent concentrated phosphoric acid. Within the area so defined, any composition selected will be found to be operative in the method hereinafter described for the chemical polishing of at least one of the metals selected from the group consisting of German silver, copper, brass, nickel, and Monel.

Although superior polishing is obtained within the range above described, in order to secure the very best results and the widest applicability in polishing, with the most desirable reaction rates and the greatest uniformity in operation, we prefer to operate within somewhat narrower limits. We have found that the range of proportions of nitric acid, acetic acid, and phosphoric acid may advantageously be kept within the narrower limits represented on the accompanying diagram by the area approximately defined by the dotted lines HI, IJ, JK, and KH, the approximate coordinates of the points being: H—10 per cent concentrated nitric acid, 10 per cent glacial acetic acid, and 80 per cent concentrated phosphoric acid; I—50 per cent concentrated nitric acid, 10 per cent glacial acetic acid, and 40 per cent concentrated phosphoric acid; J—50 per cent concentrated nitric acid, 40 per cent glacial acetic acid, and 10 per cent concentrated phosphoric acid, and K—10 per cent concentrated nitric acid, 80 per cent glacial acetic acid, and 10 per cent concentrated phosphoric acid. The preferred compositions of the baths for the chemical polishing of the hereinabove-referred to metals and alloys, with respect to the relative proportions of nitric acid, acetic acid, and phosphoric acid, lie within this second lesser area which is wholly enclosed within the broader area first defined.

By "German silver" we refer to the well-known type of nickel brass having a composition within the following approximate range in percentages by weight: copper, 50 to 70 per cent; zinc, 5 to 30 per cent; and nickel, 7 to 30 per cent. In speaking of copper, we refer not only to relatively pure copper, but also to copper that may contain minor amounts of such elements as silver, arsenic, antimony, lead, selenium, cadmium, etc. The term "brass" is intended to cover copper-zinc alloys of varying compositions containing, in general, from 55 to 95 per cent copper and from 5 to 45 per cent zinc, by weight, some of which may contain small percentages of other metals such as lead and tin. The nickel referred to may be relatively pure nickel or it may contain minor amounts of such elements as cobalt, copper, iron, carbon and manganese. The term "Monel" refers to the well-known alloys containing, approximately, from 55 to 70 per cent nickel, from 0 to 75 per cent iron, and from 20 to 44 per cent copper,

5726403
9592 conc
phosphoric

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by weight, as well as up to several per cent of other minor elements such as aluminum, manganese, etc.

As is shown by the diagram, the composition of our polishing baths has sufficient latitude to enable commercial operation without prohibitively stringent control. In general, considering only the relative proportions of the three primary components—concentrated nitric acid, glacial acetic acid, and concentrated phosphoric acid, the broad composition range may vary from about 5 to 85 per cent concentrated nitric acid, from 0 to about 90 per cent glacial acetic acid, and from 0 to about 95 per cent concentrated phosphoric acid.

Under the same conditions, the preferred composition ranges from about 10 to 50 per cent concentrated nitric acid, from about 10 to 80 per cent glacial acetic acid, and from about 10 to 80 per cent concentrated phosphoric acid.

Although the accompanying triaxial diagram shows the relative proportions of nitric acid, acetic acid, and phosphoric acid in a system consisting only of these three components, additional materials may be present. For example, a bath containing a ratio of nitric acid plus acetic acid and/or phosphoric acid selected from the diagram may, if desired, be diluted with a certain amount of water. The maximum amount of water that may be added without markedly impairing the character of the polish depends to a large extent upon the ratio of nitric, acetic, and phosphoric acids selected. For example, baths composed of nitric and acetic acids, those baths lying on the line DE of the diagram, may be diluted with as much as 25 per cent of water; however, if this concentration is greatly exceeded, there is a decided decrease in the brightness of the resulting polish. In general, we prefer to keep the water added as such to these baths below approximately 10 per cent.

On the other hand, baths composed of nitric and phosphoric acids, those baths lying along the line AB of the diagram, show a noticeable loss in the brightness of the resulting polish when much more than 10 per cent of water is added to the bath; and, in these baths, we prefer to keep the water added as such below approximately 5 per cent of the total bath volume in order to obtain the very best results. With mixtures of the three acids, the maximum desirable water additions will lie somewhere between the above-disclosed limits.

In addition, the baths also may include minor amounts of other substances such as organic compounds or other acids or salts. For example, chromium trioxide or sulfamic acid may be added to certain of the baths to minimize gassing and fuming. Such additions are particularly efficacious in the nitric acid-phosphoric acid combinations or in the baths containing relatively large amounts of nitric acid and relatively low amounts of acetic acid. We have found that acetic acid, in itself, is effective in reducing the fuming tendency of nitric acid; therefore, there is no particular advantage in adding chromium trioxide or sulfamic acid to baths containing appreciable amounts of acetic acid. In general, additions of up to about 10 per cent, based on the total weight of the bath, of chromium trioxide or of sulfamic acid are effective in minimizing fuming tendencies. For most cases, however, we prefer to add from about 0.5 to about 5 per cent of these materials.

Small additions of a wetting agent are effective in materially improving the character of the polish obtained from the bath. In general, addi-

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tions in the general range of from 0.05 to 1.0 per cent, based on the total bath weight, are effective for this purpose.

Also, the addition of traces of a chloride, such as may be added by the introduction of small amounts of hydrochloric acid, sodium chloride, etc., materially increases the brightness of the resulting polish. In general, an addition chemically equivalent to that obtained from an addition of from 0.01 to 1.5 per cent of hydrochloric acid is sufficient for this purpose. In some cases, the addition of minor amounts of various metal salts such as uranium acetate and cadmium or magnesium nitrate gives slightly improved results.

Regardless of what other nonessential ingredients may be present in the bath, however, the relative proportions that the nitric acid, acetic acid, and phosphoric acid should bear to each other may be obtained from the accompanying triaxial diagram.

Unless otherwise specified, all percentages referred to herein will be understood to represent percentages by volume rather than by weight. Also, the terms "nitric acid," "acetic acid," and "phosphoric acid" refer to the respective commercial strength concentrated acids. In other words, "nitric acid" refers to commercial nitric acid having a specific gravity of 1.42, "acetic acid" refers to commercial glacial acetic acid having a specific gravity of 1.05, and "phosphoric acid" refers to commercial phosphoric acid having a specific gravity of 1.7.

It will be understood, of course, that, within the limits of additional water referred to above, diluted acids may be used. Also, although orthophosphoric acid is specifically referred to, chemically equivalent amounts of other forms of this acid, such as metaphosphoric and pyrophosphoric, may be used. The chromium trioxide may be added as the compound CrO_3 , or chemically equivalent additions of the various chromates or dichromates may be substituted. In the same way, the salts of sulfamic acid may be substituted for the acid. In respect to the addition of wetting agents, referred to above, we have found that such agents as Nacconol NR, a sodium alkyl aryl sulfonate; Duponol ME, an alkyl sulfate, and Fixanol, a quaternary ammonium salt, and Orvus, sodium lauryl sulfate, are quite satisfactory. In cases where an addition of water is referred to, the stipulated addition in excess of that normally present as a result of the use of commercial acids is meant.

As disclosed in the accompanying diagram and discussed hereinbefore, the polishing baths of this invention are composed of nitric acid plus either acetic or phosphoric acids or a combination of the two. In general, the baths must contain at least approximately 5 per cent of nitric acid or satisfactory polishes are not obtained. Baths containing less than about 5 per cent nitric acid tend either to be inactive or to etch the metal surface. When more than approximately 85 per cent of nitric acid is present, the baths tend to be too reactive and to etch the metal surface. If more than about 10 per cent of phosphoric acid is present, the baths tend to become rather reactive when the nitric acid concentration exceeds about 75 per cent. With the higher nitric acid contents, the baths show a greater tendency toward fuming and, if the solution is too reactive, there may be a tendency for the polished surface to develop furrows.

Baths containing nitric and acetic acids, but

little or no phosphoric acid, produce quite satisfactory polishes on German silver and fair polishes on brass; however, approximately 5 or 10 per cent of phosphoric acid is required before the baths attain wide applicability. As mentioned hereinbefore, superior results are obtained with the nitric acid-phosphoric acid mixtures when either chromium trioxide or sulfamic acid is present. In the polishing of nickel or Monel, it is desirable to have at least a trace of a chloride, such as is obtained from the addition of a minor amount of hydrochloric acid, present; this is especially true in the case of nickel, as this metal shows a tendency to become passive unless a small amount of chloride is present.

When chromium trioxide, sulfamic acid, hydrochloric acid, or additional water is added to the polishing baths of this invention in an amount much exceeding the hereinbefore disclosed limits, there is a tendency for the baths to stain and to produce a smooth etch and, therefore, to give surfaces comparable with the bright dips of the prior art rather than with the mirror-like, reflecting polishes obtained by means of our invention.

In connection with the foregoing discussion of the effect of the concentration of the various components on the character of the polish, it will be understood of course that no sharp transition takes place in the nature of the bath at the indicated concentration limits. These limits merely define what may be termed a threshold zone, and the excellence of the polish and the flexibility of bath operation gradually decrease as these limits are approached and crossed.

In the method of chemically polishing German silver, copper, brass, nickel, or Monel, using a bath of a composition indicated as suitable by reference to the accompanying triaxial diagram, the specified metal or alloy, or an article having a surface of the specified metal or alloy, is merely immersed in a bath of the selected composition for a sufficient length of time to produce the desired high degree of polish on the metal surface.

The time required to produce the desired polish will depend, of course, upon the character of the original surface and upon the composition and the temperature of the bath. In general, polishing times will vary from 15 seconds to 10 minutes; however, as will be hereinafter discussed, much longer times may be used without decreasing the excellence of the polish. The bath temperature should preferably be kept below approximately 300° F., inasmuch as at higher temperatures, especially with baths containing acetic acid and phosphoric acid in the lower composition range, there is a tendency for excessive fuming to take place. Some of the disclosed baths, in fact, boil at temperatures below 300° F., and in no case should the boiling temperature be exceeded. However, for most of the baths, we prefer to operate at temperatures between room temperature, which may be considered to average approximately 65° F., and about 190° F. In fact, since only comparatively short periods of immersion, 15 seconds to several minutes, are required for polishing in many of the compositions at room temperature, there is little, if anything, to be gained by heating these baths.

It is not necessary to agitate the work when polishing in the herein disclosed baths. However, under certain conditions, especially in baths having nitric acid concentrations in the higher portion of the composition range, there may be some tendency for the polished surface to develop fur-

rows. Moderate agitation of the work is quite effective in eliminating such defects.

The polishing baths of this invention that contain appreciable quantities of acetic acid have a distinct advantage in that they are not extremely sensitive to the presence of oil and grease films on the surface to be polished. Therefore, only moderate care is required in the preparation of the surface prior to polishing in these baths. In general, it is desirable to remove any heavy scale by a normal pickling operation and, if the surface is excessively oily or greasy, to degrease it by any of the well-known methods, such as the alkaline cleaner. With this simple treatment, the surface is ready for polishing as disclosed herein. Our process may also be used to polish a surface that has previously been given a "bright dip" treatment.

The following examples are given by way of illustration to show the operation of our chemical polishing process in connection with the disclosed metals and alloys. In describing the various finishes obtained, the following descriptive standards are used:

1. "A" polish—A highly reflective finish giving minimum distortion of the image of a distant object.
2. "B" polish—A reflective finish giving recognizable but faintly fuzzy images of objects more than an inch away. Perceptible graininess.
3. "C" polish—A reflective finish giving considerable fuzziness in the images of objects more than one inch away. Readily visible graininess.
4. "D" polish—A reflective finish which shows a blurred image. Bright but grainy.
5. "E" finish—A semi-reflective finish which shows a blurred image and is grainy but brightly and finely etched.
6. "F" etch—A slightly reflective surface which is brightly and smoothly etched. More etched than grainy.
7. "G" etch—A bright, non-reflective finish with a fine, smooth etch. This surface is typical of that produced by the bright dips of the prior art.
8. "H" etch—A non-reflective finish with an etch which is not smooth.

Example 1

A bath containing 50 per cent nitric acid and 50 per cent acetic acid was prepared. At a temperature of 70° F., this bath produced a "B" polish on German silver, containing 65 per cent copper, 25 per cent zinc, and 10 per cent nickel, by weight, in approximately 30 seconds. The sheet of German silver was then returned to the bath and allowed to remain for 25 minutes. At the end of this time, the sheet had been dissolved until only a thin foil remained; there was, however, no etching, and the surface remained in the category of a "B" polish.

Approximately 0.25 per cent of hydrochloric acid was added to the bath, and the temperature was raised to about 135° F. Under these conditions, a "C" polish was produced on another sheet of the German silver in about 30 seconds. This bath also gave a "C" polish on Monel, containing 67 per cent nickel, 30 per cent copper, and 1.4 per cent iron, by weight, in the same length of time. A surface characterized as a "D" polish was produced in about 30 seconds on a sheet of brass containing approximately 35 per cent zinc, by weight.

Example 2

Another bath, containing 20 per cent acetic acid and 80 per cent nitric acid, was prepared. A sheet of German silver, containing approximately 72 per cent copper, 10 per cent zinc, and 18 per cent nickel, by weight, was treated for one minute in this bath at a temperature of 80° F. A "C" polish was obtained, but there was some tendency for the surface to develop furrows. The specimen was re-treated for an additional minute with mild agitation. All of the tendency to furrow was eliminated. Approximately 0.1 per cent, by weight, of Nacconol NR was added to the bath, and the specimen was again immersed for approximately one minute. A "B" polish was produced.

Example 3

Another sheet of the German silver used in Example 2 was immersed in a bath containing 75 per cent acetic acid and 25 per cent nitric acid. The bath temperature was 70° F. After one minute, the surface had an "F" etch. The treatment was continued for an additional five minutes. At the end of this time, the surface had an "H" etch and was stained.

Example 4

A sheet of German silver containing 65 per cent copper, 20 per cent zinc, and 15 per cent nickel, by weight, was immersed in a bath containing 25 per cent acetic acid, 60 per cent nitric acid, and 15 per cent water. With the bath at a temperature of 130° F., a "C" polish was produced in one minute.

Example 5

A bath containing 50 per cent acetic acid and 50 per cent phosphoric acid was prepared. This bath produced no action on German silver, copper, brass, nickel or Monel.

Approximately 5 per cent of nitric acid was added to the bath, making the composition approximately 5 per cent nitric acid, 47.5 per cent acetic acid and 47.5 per cent phosphoric acid. This bath produced a "C" polish on the German silver containing 18 per cent nickel, by weight, in one minute at about 140° F.

Approximately 0.5 per cent of hydrochloric acid was added to this bath. With the bath temperature at about 140° F. and with a treatment time of about one minute, a "D" polish was produced on copper, and a similar polish was produced on a brass containing about 15 per cent zinc, by weight. Under these conditions, a "C" polish was produced on a sheet of Monel containing approximately 60 per cent nickel and 40 per cent copper, by weight.

Example 6

A bath containing 10 per cent nitric acid and 90 per cent phosphoric acid was prepared. About 1 per cent, by weight, of chromium trioxide was added as sodium dichromate. With the bath at room temperature, a surface characterized as a "D" polish was produced in 5 minutes on a sheet of German silver containing 15 per cent nickel, by weight. Approximately 0.5 per cent, by weight, of Orvus was added to the bath and the temperature was raised to 180° F. In this bath, a similar sheet of German silver was polished to a "C" polish in two minutes. This sheet was then returned to the bath and allowed to remain for 45 minutes. At the end of this time, the sheet had been dissolved until only a thin film remained; there was, however, no etching,

and the surface remained in the category of a "C" polish.

At a bath temperature of 200° F., a "C" polish was produced on a sheet of copper, with a treating time of 2 minutes.

A sample of yellow brass, containing approximately 35 per cent zinc, by weight, was treated for 3 minutes in this bath at a temperature of 195° F. A "C" polish was produced. This sheet was then returned to the polishing solution for 45 minutes. At the end of this time, only a thin foil remained, but the surface was still characterized as a "C" polish.

The bath temperature was raised to 265° F., and a sheet of nickel was treated for 3 minutes. A "D" polish was obtained. Approximately 1.0 per cent, by weight, of sodium chloride was added, and a "C" polish was produced on a similar sheet in the same length of time.

A sheet of Monel, containing approximately 67 per cent nickel, 30 per cent copper, and 1.4 per cent iron, by weight, was treated in this bath for 3 minutes at a temperature of 215° F. A "C" polish was produced.

Example 7

A bath having the following composition was prepared: 75 per cent nitric acid and 25 per cent phosphoric acid. A sheet of German silver containing 18 per cent nickel, by weight, was treated in this bath for 3 minutes at a temperature of 160° F. A surface characterized as a "D" polish was produced. The bath showed a pronounced tendency toward fuming. Approximately 3 per cent, by weight, of sulfamic acid and 0.3 per cent, by weight, of Fixanol were added to the bath. At a temperature of 110° F., a "C" polish was produced in approximately 5 minutes on another sample of the German silver and on a sample of yellow brass similar to that used in Example 6. The addition of sulfamic acid was increased to 6 per cent, by weight, but the character of the polish obtained was relatively unchanged. Additions of either 3 or 6 per cent of the sulfamic acid were effective in reducing the fuming tendency of the bath.

Example 8

German silver, containing 10 per cent nickel, by weight, and red brass, containing 15 per cent zinc, by weight, were treated for approximately 1 minute in a bath containing 50 per cent nitric acid and 50 per cent phosphoric acid. With a bath temperature of 130° F., a "C" polish was produced on both materials.

Example 9

A bath containing 80 per cent nitric acid, 10 per cent acetic acid, and 10 per cent phosphoric acid, at a temperature of 90° F., showed a marked tendency to produce an "H" etch on the surface of German silver, copper, brass, nickel and Monel. The bath action was very violent.

Example 10

A bath containing 80 per cent nitric acid, 15 per cent acetic acid, and 5 per cent phosphoric acid, at a temperature of 90° F., produced a "C" polish in 30 seconds on a German silver similar to that used in Example 8.

Under similar conditions this bath produced an "H" etch on copper and a "D" polish on yellow brass. The bath apparently did not attack nickel and produced a "D" polish on Monel containing approximately 70 per cent nickel and 30 per cent copper, by weight.

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Approximately 0.01 per cent of hydrochloric acid was added to the bath, and the temperature was raised to 130° F. Under these conditions, a "C" polish was produced on German silver, brass and Monel. Copper obtained an "H" etch and an "E" finish was formed on nickel.

Example 11

A bath composed of 70 per cent nitric acid, 15 per cent acetic acid, and 15 per cent phosphoric acid, with a treating time of 30 seconds at a temperature of 90° F., produced a "C" polish on German silver and on yellow brass, a "D" polish on Monel, and an "H" etch on copper and nickel.

Approximately 0.25 per cent of hydrochloric acid was added to this bath and the temperature was raised to 120° F. With a polishing time of 30 seconds, a "B" polish was produced on German silver, a "C" polish on brass, and a "D" polish on copper and Monel. Nickel was given an "H" etch.

Example 12

A bath containing 65 per cent nitric acid, 5 per cent acetic acid, and 30 per cent phosphoric acid was prepared. At 90° F., with a polishing time of 30 seconds, a "C" polish was produced on German silver containing 10 per cent nickel, by weight. Under similar conditions, a "D" polish was produced on red brass containing 15 per cent zinc, by weight.

About 1.0 per cent, by weight, of sodium chloride and 5 per cent of water were added to the bath, and the temperature was raised to approximately 125° F. Under these conditions, a treatment for 30 seconds produced a "B" polish on the German silver, a "C" polish on copper and on the red brass, and a "D" polish on Monel containing 60 per cent nickel and 40 per cent copper, by weight. Nickel was given an "H" etch.

Example 13

A polishing bath containing 20 per cent nitric acid, 25 per cent of acetic acid, and 55 per cent of phosphoric acid was prepared. About 0.1 per cent, by weight, of Duponol ME and 0.5 per cent of hydrochloric acid were added. At room temperature, and with a treating time of 4 minutes, this bath produced a "B" polish on German silver containing 15 per cent nickel, by weight, a "C" polish on copper; a "B" polish on brass containing 35 per cent zinc, by weight, a "D" polish on nickel; and a "D" polish on Monel containing 67 per cent nickel, 30 per cent copper, and 1.4 per cent iron, by weight.

The bath temperature was raised to 190° F. and the polishing time was increased to 5 minutes. Under these conditions, a "B" polish was produced on the German silver, a "B" polish on copper, a "C" polish on the brass, and a "C" polish on the nickel and the Monel.

Example 14

Approximately 0.25 per cent, by weight, of Nacconol NR was added to a bath containing 20 per cent nitric acid, 40 per cent acetic acid, 39.5 per cent phosphoric acid, and 0.01 per cent hydrochloric acid. At 190° F., a "C" polish was produced on German silver containing 10 per cent nickel, by weight; a "B" polish was produced on copper; a "B" polish was produced on red brass; and a "C" polish was produced on nickel and on Monel containing 60 per cent nickel and 40 per cent copper, by weight.

Each of the metals was treated in the bath

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until only a thin foil remained. In no case was the character of the polish materially changed.

Example 15

5 A polishing bath composed of 40 per cent nitric acid, 30 per cent acetic acid, and 30 per cent phosphoric acid was prepared; to this bath was added 0.25 per cent of Orvus and 1.0 per cent of sodium chloride, both by weight. Upon treatment for 4 minutes at 150° F., this bath produced a "B" polish on German silver containing 15 per cent nickel, by weight, and "C" polishes on copper, red brass, nickel, and Monel containing 70 per cent nickel and 30 per cent copper, by weight.

15 Approximately 15 per cent of water was added to the bath and the above-outlined tests repeated. The character of the polishes was unchanged.

Example 16

20 A sheet of German silver containing 15 per cent nickel, by weight, was treated for 2 minutes at 150° F. in a bath composed of 50 per cent nitric acid, 40 per cent acetic acid, and 10 per cent phosphoric acid. A "B" polish was produced. A similar sheet of the German silver was covered with a light film of oil and treated under the same conditions. A "B" polish was again obtained.

30 These examples are given merely to illustrate the principles, compositions, and methods of our invention, and it will be understood that variations are possible within the scope of the appended claims.

35 From the foregoing description of our invention, it will be apparent that we have provided a novel polishing bath and a method whereby the same may be used to produce highly reflective, lustrous polishes on German silver, copper, brass, nickel, and Monel. The reflectivity of the surfaces polished by means of our bath and method is superior to that produced by means of the "bright dips" of the prior art, the surfaces produced by the latter having a rating approximating a "G" etch on the hereindisclosed scale. It will also be apparent that the operation of our chemical polishing baths is much more flexible than that of the bright dips, which are extremely critical to such factors as composition, temperature, and polishing time. Furthermore, water, in addition to that present as a result of the use of commercial strength acids, may be added. This tolerance is of particular importance in that articles to be polished do not have to be thoroughly dried prior to insertion in the polishing bath.

As disclosed hereinbefore, sulfamic acid may be used in place of chromium trioxide; we therefore wish it to be understood that in claims specifying chromium trioxide, we can substitute sulfamic acid in place of the chromium trioxide, and we wish to cover this.

Having thus described our invention, what we claim is:

65 1. A bath for chemically polishing metal surfaces, which consists essentially of a mixture of concentrated solutions of nitric acid of about 1.42 sp. gr., phosphoric acid of about 1.7 sp. gr., and acetic acid of 1.05 sp. gr., which are present in relative percentages by volume lying within the area defined approximately in the accompanying diagram by the solid lines AB, BC, CD, DE, EF, FG, and GA.

70 2. A bath for chemically polishing metal surfaces, which consists essentially of a mixture of

concentrated solutions of nitric acid of about 1.42 sp. gr., phosphoric acid of about 1.7 sp. gr., and acetic acid of 1.05 sp. gr., which are present in relative percentages by volume lying within the area defined approximately in the accompanying diagram by the dotted lines HI, IJ, JK, and KH.

3. A bath for chemically polishing metal surfaces, which consists essentially of water not to exceed 10%, and a mixture of nitric acid having a specific gravity of about 1.42, phosphoric acid having a specific gravity of about 1.7, and acetic acid having a specific gravity of about 1.05 in which the relative percentages by volume of these three acids lie within the area defined approximately in the accompanying diagram by the solid lines HI, IJ, JK, and KH.

4. A bath for chemically polishing metals consisting essentially of nitric acid, acetic acid, phosphoric acid and water, in amounts varying from about 10 to about 50 per cent commercial nitric acid having a specific gravity of about 1.42, from about 10 to about 80 per cent glacial acetic acid having a specific gravity of about 1.05, from about 10 to about 80 per cent commercial phosphoric acid having a specific gravity of about 1.7, and up to about 10 per cent water, said percentage all being by volume.

5. A bath for the chemical polishing of metal, which consists essentially of nitric acid having a specific gravity of about 1.42, acetic acid having a specific gravity of about 1.05, phosphoric acid having a specific gravity of about 1.7, and water in an amount up to about 10 per cent of the total volume of the bath, the above named acids being present in the relative percentages by volume lying within the area defined approximately in the accompanying diagram by the solid lines AB, BC, CD, DE, EF, FG, and GA.

6. The method of treating metal surfaces of the group consisting of German silver, copper, brass, nickel, and Monel to produce bright polishes thereon, which comprises immersing the surface to be polished in a bath consisting essentially of a mixture of concentrated solutions of nitric acid of about 1.42 sp. gr., phosphoric acid of about 1.7 sp. gr., and acetic acid of about 1.05 sp. gr., the relative proportions by volume of these three ingredients lying within the area defined approximately in the accompanying diagram by the solid lines AB, BC, CD, DE, EF, FG, and GA, at a temperature of less than 300° F. and

for a sufficient time to effect the desired degree of polish.

7. A method of producing a bright polish on metal surfaces of the group consisting of German silver, copper, brass, nickel, and Monel which comprises immersing the surface to be polished in a bath consisting essentially of a mixture of concentrated solutions of nitric acid of about 1.42 sp. gr., phosphoric acid of about 1.7 sp. gr., and acetic acid of about 1.05 sp. gr. present in the relative proportions by volume lying within the area defined approximately in the accompanying diagram by the dotted lines HI, IJ, JK, and KH, at a temperature of less than about 190° F. and for a sufficient time to effect the desired degree of polish.

8. The method of producing a brilliant, reflective surface on a metal selected from the group consisting of German silver, copper, brass, nickel, and Monel, which comprises immersing the metal surface to be polished in a bath consisting essentially of a mixture of concentrated solutions of nitric acid of about 1.42 sp. gr., phosphoric acid of about 1.7 sp. gr., and acetic acid of about 1.05 sp. gr. present in relative proportions by volume lying within the area defined approximately in the accompanying diagram by the dotted lines AB, BC, CD, DE, EF, FG, and GA, and containing up to about 10% water.

HENRY A. HOLDEN PRAY.

IVER IGELSRUD.

GERALD L. SIMARD.

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