

and gave a strong test for PO_4 . The precipitate was washed twice by decantation with alcohol (1:1) then transferred to a filter and washed again with alcohol (1:1) till free of chloride; it was then dried in a water oven and analyzed.

The dried precipitate possessed a green color, considerably lighter than that of any of the chromium compounds already mentioned.

Analysis gave:

	Found Per cent.	Calculated for $\text{Na}_2\text{HPO}_4 \cdot 2\text{CrPO}_4 \cdot 5\text{H}_2\text{O}$ Per cent.
Cr.....	19.45	19.77
P	17.56	17.68
Na	8.79	8.75

These results fully confirm the supposition to which the results of Bloxam's basic chromium phosphate lead, *viz.*, that the addition of disodium phosphate to a solution of chromium chloride precipitates a double phosphate of chromium and sodium, which readily hydrolyzes on excessive washing with water to a basic phosphate.

In conclusion I wish to acknowledge my indebtedness to the late Prof. E. H. Miller for suggestions in the early stage of this work and also to express my thanks to Prof. H. C. Sherman, Prof. J. L. R. Morgan and Dr. F. Metzger for valuable assistance.

QUANTITATIVE LABORATORY,
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THE ANNEALING OF STERLING SILVER.

BY WM. H. WALKER.

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It was early found by the workers in metallic silver that the ware made from an alloy of copper and silver was superior in almost every respect to that made from pure silver. Although quite a wide variation in the relative amounts of these two metals can exist and still produce a usable alloy, that proportion which has been accepted as a standard and which is called "Sterling" is composed of 7.5 per cent. copper and 92.5 per cent. silver. As is the case with other alloys, Sterling silver suffers a change in its physical properties when subjected to mechanical treatment such as rolling, drawing, stamping, etc., becoming hard, stiff and brittle. When the alloy is annealed by heating it to low redness, these undesirable properties doubtless due to molecular strains, disappear, and the ware may be subjected to further mechanical treatment. These frequent heatings produce on the alloy a scale of black copper oxide which so long as the articles were finished by hand was entirely removed by the subsequent filing and buffing necessary to produce the required polished surface. When the more modern methods of rolling and stamp-

ing were introduced, a very much less severe treatment on the buffing wheels was necessary to produce the desired polished surface, and consequently the silver was removed to a very much less extent. Under these circumstances there appeared upon the finished ware a dark sheen or reflex which greatly diminished the luster and market value of the goods. This undesirable appearance is called by the workmen "fire surface" and is found to penetrate the silver alloy to a distance roughly proportionate to the number of times the alloy has been annealed. In order to remove this "fire surface" it is necessary to place the ware in strong nitric acid and dissolve away the alloy until the darkened portion has disappeared. This entails a loss to the manufacturer both from the silver dissolved and the danger of deep pitting due to the irregular action of the nitric acid.

A cause for the appearance of this black surface layer may be found in the supposition that copper oxide is formed within the silver alloy and that when the surface is polished, the minute segregated portions of copper oxide give rise to the "fire surface". As the depth of this blackened layer is at times very considerable, it is necessary to assume that the oxygen of the air penetrates the silver even at so low a temperature as 500° C. Although the solution of oxygen in molten silver has been carefully studied, the only reference to the absorption of oxygen by silver at low temperatures, found in the literature, is to the effect that below the melting point, no appreciable absorption occurs.

It required but a very simple experiment to prove that not only does Sterling silver absorb oxygen from the air but that this absorption commenced at a temperature below 500°. Of Sterling silver in the form of machine turnings, 10.2 grams heated in a glass tube in an atmosphere of oxygen, absorbed 135 cubic centimeters of the gas. The amount required to transform the copper present in the alloy into copper oxide was found by calculation to be 134 cubic centimeters.

The eutectic alloy of copper and silver has a percentage composition of 28 parts of copper and 72 parts of silver. Sterling silver, therefore, considered metallographically, may be looked upon as being composed of small bodies of the silver-copper eutectic imbedded in pure silver. If these portions of pure copper are converted into black copper oxide during the annealing process, they should be discernible when an annealed specimen is viewed under the microscope. Fig. 1 represents the polished cross-section of a fork tine which has been subjected a relatively large number of times to the annealing process. The depth to which oxygen has penetrated is distinctly shown by the dark patches of copper oxide-silver eutectic.

There is therefore no doubt as to the cause of "fire surface," and a process to anneal Sterling silver without the formation of this black layer

must be one which can be carried on in an atmosphere containing little or no oxygen.

The most easily available artificially maintained atmosphere relatively free from oxygen is found in illuminating gas. A small annealing oven was therefore constructed in which could be maintained an atmosphere of carburetted water gas during the time the silver ware was exposed to the heat. The pigs or bars of Sterling silver were when in that form annealed in an open furnace, and when reduced to sheet metal the annealing was completed in this oxygen-free oven. The finished ware was found to contain no oxide. It had acquired, on the other hand, a peculiar velvety appearance which was removed with great difficulty when the article was polished. Examined under a microscope, this appearance was seen to consist of and be caused by minute blisters. When a piece of *pure* silver, that is, free from copper, was treated in a perfectly analogous way, no blisters were produced. Pieces of regular Sterling silver which had at no time been exposed when hot to an atmosphere containing oxygen, also showed no blisters. On the other hand, a piece of Sterling silver containing "fire surface" as shown in Fig. 1, after being exposed to the hot illuminating gas, largely lost its characteristic black band and appeared as in Fig. 2. It appears as if the hydrogen or hydrocarbon gases had penetrated the silver and reduced the copper oxide to metallic copper with the formation of water. This water vapor seems to have been unable to penetrate the silver and accumulating below the surface, caused the formation of the small blisters.

When ware annealed in this atmosphere of carburetted water gas was taken to the soldering room another difficulty was met. It may be said in explanation that hollow silver ware such as tea-pots, coffee urns, mugs, etc. are frequently decorated by soldering to the plain body, strips of silver beading or edging, by means of a small gas blow-pipe. It was found that wherever the tip of the oxidizing flame touched the ware annealed in the atmosphere of reducing gas, blisters were formed. The only explanation which I can assign for this phenomenon is, again, that water vapor is not able to penetrate silver as rapidly as can either hydrogen or oxygen. Hydrogen is doubtless excluded or adsorbed by the silver during the process of annealing, and when the oxygen carried by the blowpipe flame impinges upon the hot surface, it also penetrates the silver, and uniting with the hydrogen, forms water vapor, which owing to the pressure generated forms the blisters. This theory is further substantiated by the following fact—If a piece of this annealed ware be very slowly heated in the air and then soldered, no blisters appear. In this case the oxidation of the hydrogen takes place slowly and the water vapor is able to escape. If such a piece be rapidly heated, blisters of



FIGURE 1

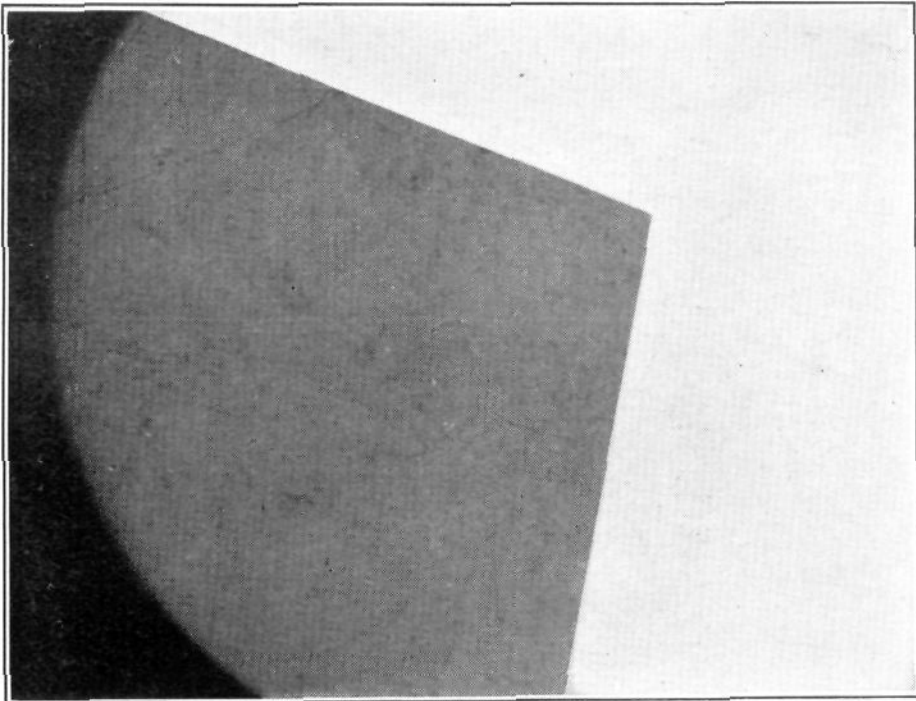


FIGURE 2

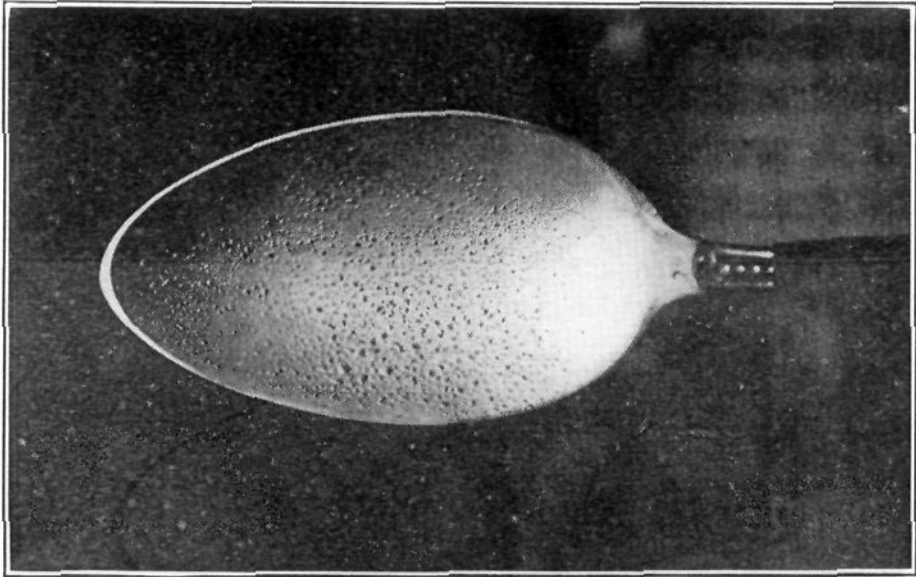


FIGURE 3

very considerable size may be formed. Fig. 3 shows a spoon which has been annealed in water gas and then plunged into the tip of a large Bunsen flame. The figure is of the natural size.

It was thus made evident that in order to successfully anneal the ware, not only must the penetration of oxygen be prevented but also the penetration of reducing gases. Experiment showed that hydrogen, methane, acetylene, etc. were very active in producing blisters, while nitrogen and carbon dioxide were entirely inert. Carbon monoxide lay between the two extremes. Further work indicated that the most desirable atmosphere from a technical point of view was one which contained enough reducing gases such as hydrogen, methane, or carbon monoxide, to prevent the penetration of the small amount of oxygen which cannot be excluded when working with large furnaces, and enough inert gas, such as carbon dioxide or nitrogen, to prevent the penetration of the reducing gases. Such an atmosphere can be prepared in an apparatus such as is employed in making so-called producer gas, when so operated as to deliver a product consisting approximately of two thirds carbon dioxide and nitrogen and one-third carbon monoxide, with a small amount of hydrogen. Annealing processes based on the above observations are now employed in practically all the large silver producing factories in America.

I wish to acknowledge the constant interest and support in this work received from Mr. C. E. Cole, President of the Towle Manufacturing Company, Silversmiths, Newburyport, Massachusetts, and from Mr. Martin Boyle, sometime chemist of the same firm.

THE RAPID DETERMINATION OF NICKEL IN THE PRESENCE OF CHROMIUM, IRON AND MANGANESE.

BY C. M. JOHNSON.

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In applying the method of T. Moore¹ to the determination of nickel in steel, the directions given on page 183, Analysis of Steel Works Materials by Brearley and Ibbotson were followed: One gram of steel was dissolved in a 150 cc. beaker with ten cc. of concentrated hydrochloric acid diluted with an equal volume of water.

When action ceased ten cc. of nitric acid (1.20) were added and the contents of the beaker were boiled to about one half. 16 cc. of dilute sulphuric acid were poured into the solution and also three grams of powdered citric acid. The solution was stirred until the citric acid was dissolved, transferred to a 600 cc. beaker, and rendered faintly but distinctly ammoniacal.

The nickel was titrated with a standard solution of potassium cyanide

¹ Chemical News, 72, 92.