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PLATED POROUS MATERIALS AND METHOD OF MAKING THE SAME

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Fig. 1.

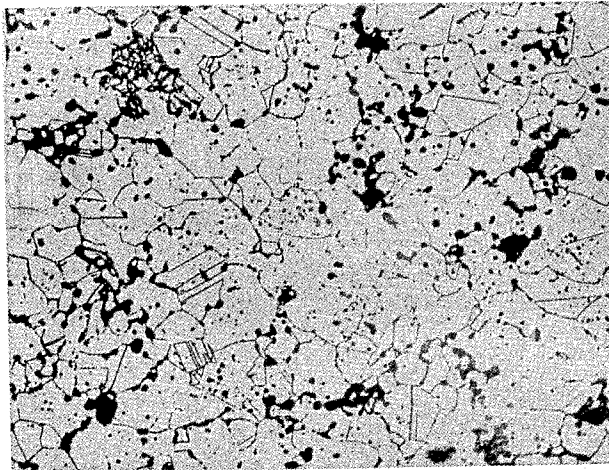
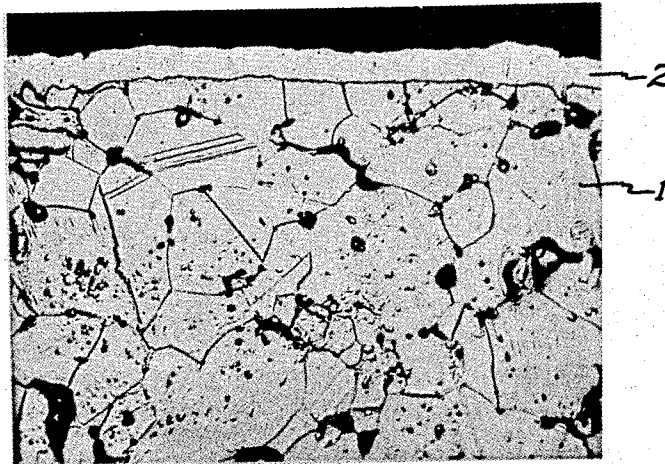


Fig. 2.



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PLATED POROUS MATERIALS AND METHOD OF MAKING THE SAME

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9 Claims. (Cl. 29—191.2)

The present invention relates to the plating of metallic materials, and more particularly, to the electroplating of porous metallic materials such as powder metallurgy bronze parts to retard corrosion of such parts.

The use of parts made by powder metallurgy techniques has increased enormously during the past years due, among other reasons, to the fact that such parts need little or no machining and can be easily pressed into desired form. However, such powder metallurgy materials present numerous problems in electroplating parts made therefrom, these being much more difficult to plate than the same parts made by more conventional methods of manufacture. The surface of the powder metallurgy part is characterized by sharp projections and deep depressions, exaggerated even when compared with a deeply etched surface. When this surface is plated, the plate usually lacks continuity. Further, the thickness of the plate as estimated by current density calculations is low in comparison to the measured thickness because of the exaggerated real area as distinguished from the apparent area. Other difficulties reside in the face that the porosity of the piece allows the electrolyte from the cleaning or plating solutions to flow into the connecting channels within the piece. Since these solutions, which are often corrosive, cannot be removed by ordinary rinsing methods, interior corrosion occurs in time. Thereafter, the trapped residual electrolyte may diffuse out through pores or absorb moisture from the air. This yields the familiar "spotting out" effect which is usually the forerunner of serious corrosion.

Various attempts have been made heretofore to avoid such corrosion in plated porous materials. Extensive rinsing and neutralization of the entrapped electrolyte has been suggested. Buffing of the surface of the part prior to plating has also been proposed. Another prior method involved impregnation with molten metal to close the pores. However, these procedures as well as other expedients attempted have not proved satisfactory, due either to unsatisfactory results in corrosion resistance or high cost.

It is therefore an object of the present invention to provide plated porous parts which are highly resistant to corrosion.

It is another object of the invention to provide a method of plating porous materials such as formed by powder metallurgy methods which is simple and inexpensive and yet effective to produce corrosion-resistant parts.

In accordance with the present invention, porous articles are successfully plated to produce a highly corrosion-resistant material by impregnating the porous base material with oil before plating the surface of the material. The method thus employed in the invention constitutes a marked departure from the previous procedures, particularly since it has been generally accepted that to efficiently plate any material the material must be free of all oil and grease. We have found, however, that contrary to previous theories excellent electroplates are

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achieved with oil impregnation of the base material and, furthermore, that the oil impregnant serves a particularly useful purpose in enhancing the corrosion resistance of the plated part. Accelerated corrosion tests that have been made show that the corrosion resistance of tin-plated porous bronze parts is at least equally as good as a tin-plated part machined from a solid forged bar.

The invention will be better understood from the following description taken in conjunction with the accompanying drawing, in which:

Fig. 1 is a photomicrograph (magnification 200X) of a cross-section of a powder metallurgy bronze part, in which the density of the material is about 90% compared to solid bronze of the same composition; and

Fig. 2 is a photomicrograph (magnification 500X) of a similar part which has been tin-plated by the present oil impregnation method.

As will be seen from Fig. 1, a powder metallurgy part is characterized by numerous pores, hollows and voids, many of which are interconnected by cracks or channels. It is this interconnected port system into which the electrolyte from the plating bath enters and thereafter leads to corrosion of the material due to inability to remove the residual electrolyte from the voids even by thorough rinsing methods. It appeared that if such diffusion of the electrolyte into the pores of the sintered powder alloy during cleaning and electroplating could be prevented, "spotting out" after plating could be eliminated. It was on this basis that the present invention was conceived.

In a process in accordance with the invention, a sintered bronze part made of pressed bronze powder was selected to be plated which had a density of 7.4 as compared with 8.2 for a wrought bronze of the same composition. Thus, the part had approximately 90% density. The chemical composition of the bronze alloy was:

	Percent
Copper	95.0
Tin	4.8
Lead	0.09
Zinc	0.07
Iron	Less than 0.01

Oxides and other objectionable surface films were first removed from the bronze part by grit-blasting with a fine abrasive. The parts were then immersed in a lubricating oil at 100° C. and allowed to remain in oil until the oil cooled to room temperature. The time of immersion did not appear critical and it seems that the oil could as well be cooled artificially. After arrival at room temperature, the parts were removed and allowed to drain. The external oil was removed by agitation in a mild soap solution at 50° C. The parts were then rinsed in cold water and plated. The plating was carried out in the conventional sodium stannate bath at about 30° C. and at a current density of 0.4 ampere per piece. This would be equivalent to a current density of about 40 amperes/ft.² on the basis of the apparent area. It should be emphasized, however, that the current on an area basis is not significant, as the measured surface area is quite different from the real area. A voltage was applied between anode and cathode before the parts were suspended in the plating bath, so as to insure immediate coverage with in. The plating was allowed to continue until a thickness of 0.0010" to 0.0015" was achieved.

In testing the electroplates obtained from the above process, the following tests were used:

(1) "Spotting out." If the electroplate is allowed to stand at room temperature in an ordinary atmosphere,

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"spotting out" will commence within a relatively short time if there is residual electrolyte trapped in the pores.

(2) Staining test. If the part is sectioned, the staining of the cut face brought about by the moisture in the air and the residual electrolyte in the pores of the metal is a measure of the latter.

(3) Microscopic examination of sections normal to the surface to reveal the continuity and the uniformity of the plate.

No "spotting out" was observed on samples plated by the above method, nor did sectioned samples stain when their cut surfaces were exposed to the laboratory air for several months.

On several samples up to 0.003" of tin was deposited. These specimens were heated up to the melting point of tin without blistering, indicating a plate of good adherence. At the raised temperature, oil was driven out from the interior of the sample through pores in the tin plate. It appeared from this that the oil within the sample serves as a reservoir which will supply oil to the pores when the sample is heated.

Fig. 2 shows a greatly magnified section of an oil impregnated and tin-plated sintered powder bronze piece 1 produced in accordance with the present process. The continuity and uniformity of the tin plate 2 is obvious from the figure. The voids and pores in the bronze base 1 are filled with oil, which gives the improved results in corrosion resistance described herein.

The important property of the electrodeposited tin produced by this process is that of the protection which it offers a sintered powder bronze part in service, as for example when assembled in a terminal and mounted outdoors on an electrical apparatus such as a transformer. A sintered bronze part of pressed powder is cheaper than a cast or forged bronze part of the same composition since the pressed part usually does not require the machining operations necessary to finish solid parts. Usually, however, plated powder metallurgy parts are less resistant to corrosion than the same part cast or wrought. Moreover, accelerated galvanic corrosion takes place when an aluminum cable is clamped against this sintered powder bronze part in assembly.

The protection against corrosion offered by the electrodeposited tin was demonstrated by salt spray tests wherein a terminal was assembled with a sintered powder bronze part and with a solid bronze piece machined from a bar of the same composition as the powder metallurgy bronze material. The bronze articles tested were parts of a high voltage terminal for a distribution transformer, the parts being known as "travelers" and constituting spring loaded clamping members used for holding an electrical conductor against the body of the transformer terminal. Terminals assembled as they would be on a distribution transformer were exposed for 360 hours in the standard salt spray test using a 20% salt solution. Examination of these parts after that length of time showed that the protection afforded by the electrodeposited tin was just as good when plated over the powder bronze part as over the wrought bronze piece.

In a salt spray test of an assembled terminal including aluminum wire and a plated bronze powder traveler not impregnated with oil wherein the exposure was for 288 hours, the aluminum wire fell apart as a result of galvanic corrosion induced by contact with the traveler. In a similar test lasting for 360 hours in which an oil impregnated powder traveler was used, the tested aluminum wire had a strength of 74 pounds.

In general, a tin plated powder metallurgy bronze object that has been treated in accordance with the present invention will withstand at least 100 hours in a salt spray test carried out in accordance with ASTM Spec. B117-49T before any substantial corrosion of the electroplate is apparent and 1000 hours before the base metal will corrode.

Other corrosion tests carried out on the parts included

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a sulphur cabinet test in which the plated parts were exposed to gaseous combustion products of natural gas and carbon disulfide, and a cyclic humidifying test.

In all of the above tests, the oil impregnated plated powder parts showed a resistance to corrosion which was equal to the plated parts machined from solid stock. Visual observation of the quantity of corrosion products at the tin-aluminum interface and tensile tests of the aluminum wire showed that galvanic corrosion was not accelerated in the oil impregnated powder parts as compared with the solid parts.

These samples were on test at a relatively constant temperature. In service where a terminal will run at a temperature higher than the atmospheric temperature, the oil in the plated powder part impregnated in accordance with the invention will diffuse out through the pores of the plate and spread over the surface, thus enhancing the corrosion resistance of the powder part and thereby reducing galvanic corrosion.

In the plating process of the present invention, an important factor is the nature of the oil impregnant, and particularly the viscosity of the oil. While it is possible to obtain satisfactory results with the use of almost any inert hydrocarbon oil such as petroleum and lubricating oils, it is preferable to employ such oils which have a viscosity within certain limits. The use of very heavy oil makes it difficult to remove the excess oil by simple draining and rinsing. It was found that a lubricating oil having a Saybolt universal viscosity of 185-255 seconds at 130° F. represented the upper limit of suitable viscosity, this range of viscosity being equivalent to SAE #30 and being just below SAE #40 which begins at 255 Saybolt seconds at 130° F. It would not be desirable to use an oil with a higher viscosity than this and preferably a lower one should be used for the impregnation step.

Another more suitable oil tested was a lower viscosity oil having a viscosity of 100-110 Saybolt seconds at 100° F. Another oil of even lower viscosity, toluene, was used and found satisfactory, this oil having a viscosity of 0.6 centistoke at 78° F. However, toluene has a rather low flash point (105° C.) so that risk would be involved in its use under temperature conditions tending to ignite it. Therefore, the viscosities of oils with flash points 50-100° C. higher than the temperature at which they will be used (100-150° C.) would preferably define the lower limit of viscosity.

A particular petroleum oil which is found to be especially suitable for the present invention has the following properties:

Flash point-----	350° F.
Fire point-----	390° F.
Viscosity, Saybolt Universal at 100° F.---	100-110 sec.
Pour point-----	-40° F.
Neutralization No. (mg. of 0.1 N KOH/g.) -----	0.04
Color class-----	2

While the above procedures were carried out in tin plating a sintered porous bronze part, it should be understood that the process is general in nature and is adapted for electroplating a wide variety of materials and articles formed usually from the powder of various metals by known powder metallurgy techniques. As the density of the part and the size of the pores encountered will vary considerably, slight modification of the process could be made within the scope of the invention to produce optimum conditions. General conditions are given below that should be met in order to insure successful plating in accordance with our invention.

A fairly stable oil should be used which is water insoluble, and in the claims the term "oil" is used in the generally accepted sense of being water insoluble. It is desirable to choose an oil of low viscosity index, since an oil having such a characteristic undergoes a relatively

great change in viscosity with varying temperature, i. e., its viscosity would decrease considerably with increase in temperature, and vice versa. This allows rapid penetration of the oil into the pores and finer capillaries of the porous base material at the elevated temperature of the oil bath in the impregnation step, but prevents the diffusion out of the pores at the decreased temperature during the cooling period subsequent to the impregnation step and prior to the electroplating step. The viscosity index of the oil should be such that even at temperatures lower than the impregnating bath a certain amount of oil is diffused outwardly to the surface of the part during the electroplating process, as well as when the final product is in operational service.

When the oil impregnated metal part is immersed in the plating solution, the oil entrapped in the pores will begin to diffuse out due to the increase in temperature obtained in passing from a cold water rinse to a plating bath at a higher temperature. This positive pressure against the plating solution electrolyte prevents its entrance into the part. In order effectively to remove this oil from the surface of the article, the oil must be below a certain viscosity and the current density above a certain minimum in order to cause gassing at the cathode which serves to mechanically remove the surface oil. It is contemplated that if a heavier oil were used, a higher current density would be required to effect its removal.

In accordance with the invention, it is also contemplated that a vacuum impregnation process could be used, wherein a vacuum is first produced and then pressure is applied during the impregnation process, this procedure in certain cases serving to increase the amount of impregnant contained in the pores. However, it has been found that such vacuum impregnation is not necessary for the success of the present process.

The electroplating bath, such as the sodium stannate solution mentioned above, is preferably alkaline for the purpose of washing off the excess oil and the oil diffusing out through the electroplate during the electroplating process. A tin-zinc alloy plate may be deposited from an alkaline solution of mixed cyanide and stannate. Other types of plating materials may be used in accordance with the invention, such as zinc, cadmium, copper, and silver, each in an alkaline cyanide solution.

Further, base materials other than bronze can be used, as for example other copper base alloys including brass, and also sintered iron. For the purposes of the invention, it is not necessary that the base material be formed from pressed metal powders. Other porous metallic materials may also be effectively plated and made corrosion resistant by the present method.

While the present invention has been described with reference to particular embodiments thereof, it will be understood that numerous modifications may be made by those skilled in the art without actually departing from the scope of the invention. Therefore, the appended claims are intended to cover all such equivalent variations as come within the true spirit and scope of the invention.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The method of plating a porous metallic body which comprises impregnating the metallic body with a liquid consisting essentially of oil, the oil having a viscosity between 255 Saybolt seconds at 130° F. and 0.6 centistoke at 78° F., removing oil from the surface of the metallic body, and electroplating the surface of the thus oil-impregnated metallic body in an alkaline electroplating bath with a metal selected from the group consisting of tin, zinc, cadmium, copper and silver and an alloy of tin and zinc.

2. The method of plating a porous metallic body formed of a pressed metal powder and having interconnected voids therein, which method comprises im-

pregnating the porous metallic body with a liquid consisting essentially of oil so that the oil fills the interconnected voids therein, the oil having a viscosity between 255 Saybolt seconds at 130° F. and 0.6 centistoke at 78° F., removing oil from the surface of the metallic body, and electroplating the surface of the thus oil-impregnated metallic body in an alkaline electroplating bath with a metal selected from the group consisting of tin, zinc, cadmium, copper and silver and an alloy of tin and zinc.

3. The method of plating a porous bronze body formed of pressed bronze powder and having interconnected voids therein, which method comprises impregnating the porous bronze body with a liquid consisting essentially of oil so that the interconnected voids therein are filled with the oil, the oil having a viscosity between 255 Saybolt seconds at 130° F. and 0.6 centistoke at 78° F., removing oil from the surface of the metallic body, and electroplating the surface of the thus oil-impregnated bronze body with tin.

4. The method of plating a porous metallic body which comprises impregnating the metallic body with a hydrocarbon oil having a viscosity between 255 Saybolt seconds at 130° F. and 0.6 centistoke at 78° F., removing oil from the surface of the metallic body, and electroplating the surface of the thus oil-impregnated metallic body in an alkaline electroplating bath with a metal selected from the group consisting of tin, zinc, cadmium, copper and silver and an alloy of tin and zinc.

5. The method of plating a porous metallic body which comprises impregnating the metallic body with a hydrocarbon oil having a low viscosity index, a viscosity less than 185 Saybolt seconds at 130° F. and a flash point higher than about 150° C., removing oil from the surface of the metallic body and electroplating the surface of the thus oil-impregnated metallic body in an alkaline electroplating bath with a metal selected from the group consisting of tin, zinc, cadmium, copper and silver and an alloy of tin and zinc.

6. The method of plating a porous metallic body which comprises impregnating the porous metallic body with oil by immersing the body in a heated oil bath and cooling the oil bath, the oil having a viscosity between 255 Saybolt seconds at 130° F. and 0.6 centistoke at 78° F., removing excess oil from the surface of the oil-impregnated metallic body, and electroplating the thus treated oil-impregnated metallic body in a heated alkaline electroplating solution with a metal selected from the group consisting of tin, zinc, cadmium, copper and silver and an alloy of tin and zinc.

7. A corrosion resistant plated porous product comprising a porous metallic base material formed of pressed bronze powder, said porous metallic base material being impregnated with a liquid consisting essentially of oil, the oil having a viscosity between 255 Saybolt seconds at 130° F. and 0.6 centistoke at 78° F. and electroplated with a firmly adherent continuous coating of tin.

8. A corrosion resistant plated porous product comprising a porous metallic base material impregnated with a hydrocarbon oil of low viscosity index having a viscosity less than 185 Saybolt seconds at 130° F. and a flash point higher than about 150° C., said oil-impregnated base material being electroplated with a firmly adherent continuous coating of a metal selected from the group consisting of tin, zinc, cadmium, copper and silver and an alloy of tin and zinc.

9. A corrosion resistant plated porous product comprising a porous metallic base material formed of pressed bronze powder, said porous metallic base material being impregnated with a liquid consisting essentially of oil having a viscosity between 255 Saybolt seconds at 130° F. and 0.6 centistoke at 78° F. and electroplated with a firmly adherent continuous coating of a metal selected

from the group consisting of tin, zinc, cadmium, copper
and silver and an alloy of tin and zinc.

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