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METHOD OF COATING TIN COATED COPPER
WITH INDIUM

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1 Claim. (Cl. 204—35)

This invention relates generally to metal or composite metal articles having a non-porous protective surface coating or integral layer and the method of producing the same. Specifically the invention concerns the treatment of a metal surface to provide it with a continuous layer or coating which is free from pinholes and completely covers the base metal therebeneath.

The invention will be described more particularly in connection with the making of non-porous tin andterne plate, but it will be obvious that this invention is applicable for treating various types of metal or metal alloy products to eliminate pores or minute openings in the surface making it corrosion resistant.

It is well known that it is practically impossible, in spite of the utmost care, to make a perfectly continuous metal coating of tin on iron, steel, copper or the like metal. This is also true forterne coatings. When the metal coating contains imperfections, such as minute openings or pinholes, the base metal, of course, is not protected and in use is exposed to attack resulting in the ultimate failure of the material. Paint and lacquer has been used heretofore to fill up the pinholes and prevent corrosion but this treatment, at best, is merely temporary and does not satisfactorily solve the problem.

It is the principal object of this invention to provide an efficient method of rendering metal surfaces substantially continuous and free from pores or minute openings.

Another object is the production of a metal or composite article having a non-porous protective surface layer comprising indium.

A further object is the provision of a metal product wherein at least a portion of the surface is provided with a uniform continuous coating or homogeneous alloy of indium.

These and other objects and advantages will become apparent as the description proceeds and will be emphasized in the appended claim.

Tin-coated copper is in general use for making various articles and is used to a great extent in the dairy industry. The porosity of the tin-coating, however, has been a decided disadvantage because the exposed copper contaminates and spoils the taste of milk. It has been proposed to improve the continuity of the tin by electroplating over a hot dipped coating and use has been made of nickel with zinc or tin coatings followed by a heat treatment, but none of these methods have solved the difficult problem of producing a satisfactory coating.

We have discovered that pores and pinhole

openings in metal surfaces can be closed by rubbing or smearing indium or an equivalent metal over the surface and into the pores and imperfections. Preferably indium is used, however an alloy of indium may be employed or metal which is plastic enough at ordinary room temperature to be smeared into the minute openings or pores so as to seal them. In general metals having a Brinell hardness between $\frac{1}{2}$ and 8 may be used.

The method of closing pinholes in metal surfaces by "smearing" with indium, as shown by tests, is remarkably efficient. To determine the effect of applying indium as a protective coating, a 2-inch length of tinned copper tubing was plated with 0.0001 inch of indium over a 1-inch portion. After plating, the indium, which is easily spread by rubbing with the finger, was "smeared" by rubbing the same with a piece of soft cloth. A number of samples treated in this manner were tested and it was found that the application of indium as described was very effective in eliminating pinholes. By this method a copper tubing was provided having a non-porous tin-indium coating which was corrosion and wear resistant.

Further tests were made to determine the efficiency of the indium "smeared" metal coating under corrosive conditions. For making these tests a 1% lactic acid solution was used.

Samples of tinned copper tubes were plated on the inside with indium and then "smeared" by means of a soft cloth held on a stick. The tubes were then stoppered at one end and filled with lactic acid solution. For comparison an ordinary tinned copper tube, as received, was tested along with a tinned copper tubing having an electroplated coating of tin. Spectrograph analyses were made at intervals.

Below are given the results of the tests:

Coating	Test time in hrs.	Spectrographic results		
		Cu	Sn	In
Regular tinned tube...	24	Strong.....	Strong..	
	72	do.....	do.....	
0.00003" In on tinned tube—smeared.	24	Faint trace..	Nil.....	Strong.
	72	do.....	do.....	Do.
0.00012 In on tinned tube—smeared.	24	Nil.....	do.....	Do.
	72	Faint trace..	do.....	Do.
0.00012 Sn on tinned tube—smeared.	24	Strong.....	Strong..	
	72	do.....	do.....	

The test results clearly indicate the remarkable effect produced by the use of indium as compared with tin and further that indium coatings of 0.00003" thickness were equally as good as an indium coating four times as thick.

After the above tests were finished the tubes were split and examined. The tin coatings were heavily etched while the indium coated samples were substantially unattacked.

Another set of tests were conducted under more or less the same conditions except that in one case the indium was "smeared" at once, in another case seven days after plating and in the third case not "smeared" at all. A fourth sample had indium plated directly on copper with no under-coat of tin. As before a regular tinned tube was tested for comparison. The following tables give the results of this test:

Coating	Test time in hrs.	Spectrographic results		
		Cu	Sn	In
0.00010 In on tinned tube — smeared at once.	72	Low	Trace	Strong.
	144	do	do	Do.
	288	Trace	Strong	Do.
0.00011 In on tinned tube — not smeared.	72	M. S. ¹	Moderate	Do.
	144	M. S. ¹	do	Do.
	288	Low	Strong	Do.

¹ M. S. moderately strong.

Coating	Test time in hrs.	Spectrographic results		
		Cu	Sn	In
0.00011 In on tinned tube — smeared 7 days after plating.	72	Low	Trace	Strong.
	144	do	do	Do.
	288	Trace	Moderate	Do.
0.00010 In on plain copper — smeared at once.	72	do	do	Do.
	144	do	do	Do.
	288	do	do	Do.
Regular tinned tube.	72	Strong	High	Do.
	144	do	do	Do.
	288	Low	do	Do.

The last series of tests show that rubbing or smearing of the indium is an essential step in order to produce the improved results. Moreover it is relatively immaterial whether the indium is "smeared" at once or not. The test results also seem to indicate that copper builds up to a certain amount and then no further and in some instances actually decreases. In this connection it is probable that tin and indium replace copper from solution as might be expected due to their much higher position in the electromotive series of elements.

Tests made to determine the affect of indium on milk showed it to have little or no effect.

Moreover it is known that indium is non-toxic and hence is safe to place in contact with foods.

When indium is plated on top of copper, tin or other metals and then rubbed or "smeared," the pinholes and imperfections in the metal are filled producing a uniform coating. In the course of time the interdiffusion of the indium and base metal produces a homogeneous alloy which is substantially non-porous and is resistant to corrosion.

The term "smearing" as used in the specification and claim refers to overspreading of indium on the base metal surface to form a continuous unbroken layer. The "smearing" operation is distinguished from the conventional metal surface treatments such as grinding, polishing and buffing in that substantially less pressure is employed than in performing the latter operations and the object is to merely spread the metal over the surface rather than remove it.

As a modification of the process indium may be plated or otherwise coated onto the surface of the base metal after which it is rubbed or smeared to fill imperfections in the base metal and then an outer coating, i. e., tin, zinc, etc. applied over the indium. In each case the finished product comprises a pore sealing layer of indium which is essential.

It will be understood that this invention is not limited to the specific materials and uses given and that widely different embodiments of the invention may be made without departing from the spirit and scope thereof as defined in the claim.

What is claimed is:

The method of treating tin coated copper articles used for handling milk whereby small minute openings in the tin coating are sealed preventing milk from coming into contact with the copper base metal therebeneath, which consists in plating indium on said tin coating to a thickness of 0.00003 inch, thereafter rubbing the indium coating with a soft cloth so as to spread the indium into surface imperfections in the tin coating filling them so that the copper base metal is provided with a sealing layer consisting of tin and indium which is free from pinholes and minute openings such as would expose the base metal.

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