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## METHOD OF INHIBITING FORMATION OF BLACK SPOTS ON TINNED COPPER

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5 Claims. (Cl. 204—43)

This invention relates to a method of inhibiting formation of black spots on tinned copper, and this application is a continuation in part of our prior application, Serial No. 160,778, filed August 25, 1937.

For years the dairy machinery industry has used tinned copper for making milk vats, coolers, etc. Tinned copper, that is copper coated with a thin layer of tin, is liked for these articles because it is of comparatively low cost and can be handled and fabricated more easily than the substitutes, such as enamel ware, stainless steel, rich nickel alloys, etc. There is, however, one particularly serious difficulty with tinned copper which is known as black spots or tin pest. It is a serious problem in caring for dairy apparatus. This condition is not due to corrosion of the base metal but rather to an allotropic change in the tin which results in disintegration of the coating. Applicants' method prevents or greatly hinders this allotropic change.

It is therefore an object of the present invention to prevent or delay the formation of these black spots, and we have found that this may be done by incorporating a small amount of one or more of certain other metals with the tin. We have found that when a small amount of one or more of the metals of the group consisting of nickel, cobalt, and iron are deposited with the tin, either simultaneously or successively, the formation of these black spots is materially delayed. It is thought there is a real alloy formed of tin and the other metal or metals at the surface, and that this alloy inhibits the allotropic change in the tin. Nickel, cobalt and iron have a similar effect but our tests indicate nickel is the most effective in preventing black spots.

For example, we added a cyanide to the regular sodium stannate electrolyte used for electroplating tin upon copper, dissolved nickel or nickel salts in this and then made an electrodeposit which when tested had a material improvement in resistance to formation of black spots as compared with the pure tin coating. One electrolyte contained in solution 1.135 ounces of tin per gallon, .0867 ounce of nickel per gallon and .404 ounce of cyanide per gallon. In this case the nickel and the tin were simultaneously deposited, but we have also found that the formation of the black spots is hindered or delayed if a coat of commercially pure tin is first put onto the copper and then the tin-nickel coat deposited, or we can put on the metals separately and in succession, first the layer of tin, then the other metal or metals, as nickel for example, or if desired we can add to the second coat a third coat of tin or a combination of the tin and the nickel.

As stated above we prefer nickel for this process, but we are not confined to the use of nickel. We have found that cobalt and iron when plated in combination with tin in the same manner also prevent or greatly hinder the formation of black spots.

Nor are we confined to the use of pure metals. In one instance in our tests the tin coating on one sample contained approximately 90% tin, 9% nickel and 1% iron. The point is that when tin is deposited on the copper in combination with certain other metals the black spot formation is materially hindered. We have had as high as 30% nickel present but prefer less because the coating is more ductile. The tin in the coating should greatly predominate with the other metal or metals in relatively small amount. Any small amount of the added metal assists in preventing black spot and we prefer not to use more than about ten percent as this has been found to be sufficient.

The coating is put on preferably by codeposition of the metals from a single electroplating bath, but as suggested above we have also accomplished the desired end by successive deposits from different baths, as for instance from a tin bath for ten minutes, then from a nickel bath for two minutes, and then from a tin bath for two minutes.

In another test copper was plated with cobalt and tin. The solution used was cobalt sulphate in sodium cyanide. To this was added some of the regular sodium stannate plating solution. The plating surface was a little darker than pure tin much as the nickel-tin combination is the darker. On testing this sample it was evident that this cobalt-tin deposit was considerably better than pure tin. Analysis of the coating confirmed the presence of an appreciable amount of cobalt in the tin coating but with the tin greatly predominating.

In another example copper was plated with iron and tin. In this case we used ferric sulphate, ammonium oxalate, oxalic acid, stannic chloride, and a little sodium perborate, all dissolved in water. The plating was accomplished at about 60° C. The plate was not as good looking as with the other materials, but when the material was tested it showed material improvement over the ordinary tin coating in resistance to formation of black spots. On tests of the coating iron and tin were found to be present.

The resultant coating is essentially a tin coat-

ting with a small amount of the other metal or metals which have the effect of inhibiting the allotropic change in the formation of black spots or tin pest.

We do not wish to fuse the tin coating either in depositing or after it has been deposited. Fusing a tin coating on copper definitely thins the tin coat by making the tin diffuse into the copper and thus really result in a bronze coating of mostly copper instead of a tin coating or coating mostly tin. In other words fusing of the tin coating is undesirable in our method for inhibiting black spots as our experiments have indicated it tends to reduce the resistance of the coating to this disease.

Having thus set forth the nature of our invention, what we claim is:

1. A method of inhibiting formation of black spots on tinned copper which consists in electrodepositing on the tinned surface an amount of at least one of the metals of the group consisting of nickel, cobalt and iron sufficient to inhibit black spot formation, and with the resultant coating essentially tin and of at least about 90 per cent of this metal.

2. A method of inhibiting formation of black spots on tinned copper which consists in electrodepositing on the copper a coating consisting of tin and an amount of metal of the group consisting of nickel, cobalt and iron sufficient to inhibit black spot formation, and with the resultant coating essentially tin and of at least about 90 per cent of this metal.

3. A method of inhibiting formation of black spots on tinned copper which consists in electrodepositing on the tinned surface a coating consisting of tin and an amount of metal of the group consisting of nickel, cobalt and iron sufficient to inhibit black spot formation, and with the resultant coating essentially tin and of at least about 90 per cent of this metal.

4. A method of inhibiting formation of black spots on tinned copper which consists in simultaneously electrodepositing on the copper from a single electroplating bath as a coating tin and an amount of other metal from the group consisting of nickel, cobalt and iron sufficient to inhibit black spot formation, and with the resultant coating essentially tin and of at least about 90 per cent of this metal.

5. An article of manufacture for use in handling food and beverage products, including fabricated vessels, containers or structures made at least partly of copper and an electrodeposited coating on the copper consisting essentially of tin in amount at least about 90 percent and an amount of metal of the group consisting of nickel, cobalt and iron sufficient to inhibit black spot formation, said coating being on that surface to be used in contact with the food and beverage products whereby the formation of black spots on this coated surface is inhibited.

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