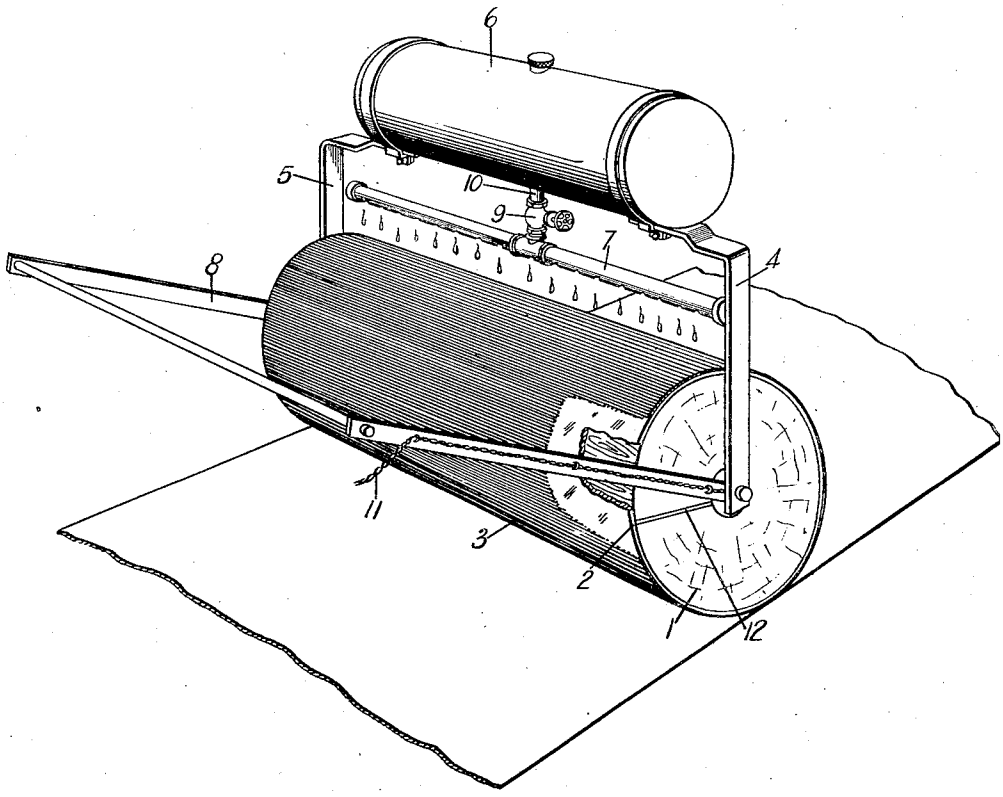
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PRODUCTION OF AN ADHERENT PATINA UPON COPPER OR ITS ALLOYS

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INVENTORS.
Clarence E. Irion.
George L. Craig.

BY
Cooper & Mahoney
ATTORNEYS

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PRODUCTION OF AN ADHERENT PATINA UPON COPPER OR ITS ALLOYS

Clarence E. Irion and George L. Craig, Columbus, Ohio, assignors to The Battelle Memorial Institute, Columbus, Ohio, a corporation of Ohio

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Our invention relates to the production of an adherent patina upon copper or its alloys. It has to do particularly with the production of the patina upon roofs of copper or copper alloy and upon other objects which cannot be immersed in a bath, though our invention is also capable of application by immersion of the article to be treated in a bath.

When bright, unprotected copper is exposed to the ordinary atmosphere, as in the case of a copper roof, its surface soon becomes tarnished, brown and then black. After a lapse, of say ten to twenty years depending on atmospheric conditions, it takes on a green or greenish-blue color, generally referred to as "patina" and considered highly desirable as a decorative characteristic.

The tarnished, brown or black appearance characteristic of the intermediate stage is considered quite undesirable, from a decorative standpoint, and considerable effort has been made to hasten the development of the patina artificially. These efforts have varied considerably and have involved spraying or rubbing the copper or copper alloy with chemical solutions which attack the metal, as well as immersing the copper or copper alloy object in a bath designed to produce the desired color both with and without electrolysis.

Experience indicates that the patina ordinarily produced by spraying or rubbing copper or copper alloy with chemical solutions which attack the metal is ordinarily non-adherent. It is either slowly soluble and therefore dissolved gradually by rain or is otherwise dislodged by the action of rain, wind, frost or changes in temperature that bring about expansion and contraction of the metal. When these temporary coatings peel off, the bare copper is exposed and is left to pass through the unsightly stage above referred to.

Some effort has been made to simulate patina by the application of greenish-blue paints. However, these also tend to peel off and repainting is required. Furthermore, it is difficult to satisfactorily simulate the natural color of patina with paint. Scientists, both in this country and abroad, have attempted to develop methods for rapidly producing patina artificially upon copper and copper alloys. In the main, they have examined the patinas from old roofs and have found them to be mainly composed of basic sulphate of copper of the definite composition $CuSO_4.3Cu(OH)_2$, which is that of the natural mineral brochantite. Since sulphur enters into this composition, it is supposed that the necessary sulphur comes primarily from sulphur-containing gases in the atmosphere due to the burning of coal. Therefore, these investigators have directed their efforts towards the treatment of copper by sulphate solutions under such conditions that a basic and insoluble copper sulphate, approaching brochantite in composition, may be formed. One such effort has consisted in immersing the copper or copper alloy to be coated in an ammonium sulphate solution of definite concentration, hydrogen ion content and temperature, and intermittently removing the copper or alloy so that the solution adhering to it comes into contact with air, with resultant oxidation and the production of a basic salt. The process is repeated until a suitable color is obtained and takes a day or more for completion. The color obtained is not a close match to the natural patina and soaking in hot water or steaming is required to produce a better match.

There are obvious difficulties in applying such a process to an immovable copper product, such as copper in place upon a roof. Among these, are the necessity for repeated application of the solution and the desirability of operating at a controlled and elevated temperature. Moreover, while it is claimed that the coating may be made so as to be adherent when subjected to weathering, some difficulty is reported in carrying out the process so as to secure satisfactory adherence. Flaking off of the coating apparently results from jarring in shipment or from very slight bending of the copper.

Some attempt has also been made to obtain the patina upon copper or copper alloys by subjecting it to anodic electrolytic treatments in a bath of sodium sulphate, sodium hydroxide and sodium cyanide. Such treatment in this electrolyte, followed by heating in a copper sulphate solution, produces a patina, but it is not adherent. Likewise, the necessity for heating renders the process impracticable for the treatment of immovable objects.

An attempt has been made to artificially produce patinas by chemically treating copper with aqueous solutions of ammonium chloride, sodium carbonate, ammoniacal copper sulphate or sodium arsenite without electrolysis. The coatings so produced, however, were not stable and discoloration resulted upon subjection of the coated article to fog.

Another method of producing a patina has involved the application of an ammonium sulphate

solution twice a day for six days, followed by the application of a solution of copper sulphate, sodium hydroxide and ammonium nitrate. The coatings so produced successfully resisted subjection to fog but peeled during the first period of frost.

Still another method suggested has consisted in an anodic electrolysis in a solution of magnesium sulphate and potassium bromate with the addition of a small amount of magnesium hydroxide. This method, however, requires that the electrolysis be carried on at an elevated temperature, approaching the boiling point of the solution. Even at a high current density, it requires fifteen minutes to produce the coating. At a low current density, as much as thirty minutes is required. Our tests of this method for the periods indicated show that the patina thus produced is quite pale in color. The time and temperature required, together with the expensive potassium bromate, render this method not fully satisfactory even for use in vats, and entirely impracticable for the production of patina upon copper or copper alloy in place, as upon a roof.

Another method that has been suggested consists in the anodic treatment of copper or copper alloys in an electrolyte of "natural carbonate water" or similar liquids effective to give off carbonic acid under the influence of an electric current. In this method, it is proposed to flow the electrolyte continuously between the electrodes, while electrolyzing at a very low current density. This method has many drawbacks which render it impracticable. The low concentration of carbonate ions in a natural mineral water electrolyte, which low concentration is accentuated by the acid nature of the solution, together with the low current density used, prolongs the operation to such an extent as to make the cost of applying the method prohibitive, even if it were possible to obtain an adherent patina. The use of a flowing electrolyte further increases this difficulty and renders the method even more impracticable for the treatment of articles in place, such as roofs of cooper or copper alloy.

We have experimented with solutions saturated with calcium and magnesium carbinates and containing dissolved carbonic acid, as in mineral waters. Electrolyzing such solutions with a copper anode at 0.1 amp/dm^2, we found that no green coating was formed in the first fifteen minutes, but finally a green color appeared and after four hours electrolysis the copper was completely covered. But the coating rubbed off at the slightest touch, merely lying on the copper and not being at all adherent. Such a coating is valueless for our purpose. For example, would completely wash off a roof at the first rain.

The prior art thus fails to provide any rapid and satisfactory method of application.

One of the objects of this invention is to provide a method for closely simulating the natural patina resulting from the prolonged weathering of copper or copper alloy which will produce a coating having the proper characteristics of color, adherence and resistance to all normal weather conditions as well as conditions of shipment, application and use.

Another object of this invention is to provide such a method which will be relatively simple in its nature and capable of application at a relatively low cost and which will permit the production of patina upon copper or copper alloys rapidly and with a minimum of difficulty.

Our method departs from those teachings of the prior art which seek to produce a basic sulphate initially and directly upon the copper or copper alloy. Instead, we initially produce a basic carbonate upon the metal by using a relatively concentrated electrolyte in conjunction with a current density sufficient to produce an adherent coating very rapidly. Moreover, instead of using a natural carbonate water and treating it under such conditions as to produce carbonic acid which tends to prevent adequate concentration of the carbonate ions, we use a rather strong solution of a soluble alkali carbonate, such as sodium carbonate, sodium bicarbonate, similar potassium carbonates, or ammonium carbonate. With such an alkaline solution we are able to obtain a high concentration of the carbonate ion and by the use of a current of comparatively high density, we have been able to bring about the rapid formation of an adherent patina upon the copper or copper alloy which is used as an anode in the electrolytic process.

Our process is applicable either by making the copper to be coated anode in a bath of the electrolyte or by effecting the electrolysis directly upon the copper or copper alloy without suspending it in a bath. In the latter case, we preferably use a metal or metal-surfaced roller covered with cloth or other absorbent and resilient material, which is kept continually moist with the electrolyte and which is supplied with an electric current of relatively high density, with the metal roller forming the cathode, while the copper or copper alloy to be coated forms the anode.

More specifically, we may use as the electrolyte a solution of an ordinary commercial sodium carbonate; the commercial sodium carbonates, soda ash, washing soda or baking soda are all cheap and effective. We prefer the baking soda, that is, sodium bicarbonate. The concentration of the carbonate solution may be varied within wide limits, without materially affecting the results. Using sodium bicarbonate, $NaHCO_3$, we have obtained good results with solutions as weak as 2% and as strong as full saturation, approximately 10%. Ordinarily, we prefer solutions of 5% to 8% sodium bicarbonate, by weight. Our preferred solutions are alkaline in nature, i. e., have a hydrogen ion concentration ("pH") well over 8.

The current density can also be widely varied. We have obtained good results with current densities as low as 1 amp/dm^2, and as high as 20 amps/dm^2, with no indication that either figure is a limiting value. In general, we prefer 1½ to 4 amp/dm^2. These current densities are the initial values. As the coating forms, the current taken by the cell, at a constant applied voltage, decreases.

The time for deposition may be made exceedingly short. Using a solution of 8% concentration in $NaHCO_3$, and a current density of 18 amps/dm^2, we obtain a satisfactory coating in less than 1 minute. With a weaker solution and lower current density, electrolysis may be continued for half an hour or more. Thus, it is possible to produce the patina in a very few minutes, while all prior art processes known to us require a considerably longer time. By a short period of electrolysis or by a low current density, or by both, a blue coating may be formed. By a longer period of electrolysis or a higher current density, or by both, a green coating may be formed.

We prefer to avoid leaving an excess of the electrolyte on the coating after electrolysis. If such an excess is left to dry on the coating, the

initial appearance may be whitish. However, this may be washed off and, if the coating is upon a roof, the sodium salt will be removed by the first rain, with the result that the patina will be of a more brilliant color.

Instead of using sodium bicarbonate, we may use sodium carbonate. However, strong solutions of sodium carbonate left on the coating without current passing, will change the coating to a brown color and, with high current densities, may produce a black color. Therefore, if sodium carbonate is used, the coating should be washed or flushed with water soon after its formation and we prefer to do this even in the case of the bicarbonate.

Ammonium carbonate may be used to form the electrolyte. It acts more rapidly than sodium bicarbonate or sodium carbonate and produces a bluer coating. However, unless a blue coating is desired, the relatively high cost of ammonium carbonate renders its use undesirable.

As pointed out above, other alkali carbonates may be used to form the electrolyte. We prefer to avoid the carbonates of the alkaline earths or the metallic carbonates, because of the generally low solubility of these carbonates and, in the case of metal carbonates, of the tendency of the metal to deposit on the cathode.

It should be noted that we do not find it necessary to heat the electrolyte and that the anodic coating is formed rapidly at ordinary atmospheric temperatures. This, together with the short time of application required, makes it feasible to apply the coating to copper or copper alloy in place.

In a crude form of such application, a cotton swab may be wound on the end of a copper rod, the rod made the cathode of a direct current circuit, the copper or copper alloy to be coated made the anode, and the swab dipped in the carbonate solution and rubbed over the metal to be coated. The copper carbonate produced by the anodic attack upon the copper and the reaction with the electrolyte of the copper ions thus formed, appears promptly on the metal surface as an adherent coating. The amount of deposition can readily be judged by eye and the deposit built up uniformly by moving the swab about.

In a more advanced form of our invention, we use a copper cathode inside a resilient roller of absorbent material that can hold the electrolyte, and roll this back and forth over the surface to be coated. Copper roofs, corrugated to provide for expansion and contraction of the copper, have been evenly coated with such rollers. Working on a small scale with a roller of the following dimensions 7" long x 2" diameter, a solution of 5% concentration in $NaHCO_3$ and an applied voltage of 30 volts, resulting in a current of about 10–20 amperes, we have coated a square foot of copper in 1 minute and less.

On a still larger scale, a roller of 18" long and 8" diameter of the same general design as above was used to coat a copper roof at the rate of about 2 sq. ft. per minute. Using a 5% solution of $NaHCO_3$, with this large roller, an adherent coating was applied on a certain area of a steeply pitched roof and records made to indicate the cost of application. This area measured 29 sq. ft. and was covered in 16 minutes. Five gallons of the solution were used, and the electrical energy used was about 2400–3200 watts. The voltage applied to the large roller was 40, and the average current drawn about 60–80 amperes. Thus, a 100 sq. ft. "square" of roofing would require about seventeen gallons of solution (7 lbs. of solid $NaHCO_3$), about 50 minutes labor of one man, and around 2½ k. w. h. The cost of application is therefore seen to be low.

The small roller may be dipped in a dish of the carbonate solution from time to time to keep it wet. We prefer to supply the solution continuously to the large rolier. A diagrammatic representation of a suitable device for application of the coating to roofs in place is shown in the drawing appended hereto. Obviously, an analogous apparatus can be made of size and shape suitable for coating gutters, down-spouts, or other irregular objects.

The form of apparatus which we preferably use in the application of our process to immovable objects is shown in the accompanying drawing wherein:

The figure represents a perspective view of our preferred type of apparatus for applying our process.

In the form of apparatus shown in the drawing, there is embodied a wooden roller 1 covered with copper 2, to distribute the current, over which is a thick cloth covering 3 and this roller is mounted between standards 4 and 5. The standards 4 and 5 carry a storage tank 6 for the electrolyte and this storage tank, in turn, carries on its lower side a spray 7 having apertures 8 for the delivery of the electrolyte onto the cloth-covered roller. A manual controlling valve 9 for regulating the supply of electrolyte to the spray may be disposed in the pipe 10 which connects the tank 6 with the spray pipe 7.

The current may be introduced by means of the connection 11 running along the handle and led by the metal axle and the lead 12 to the copper covering of the roller and thence to the cloth pad. Any suitable connection (not shown) may be provided for the metal upon which the coating is being produced. Direct current is preferably supplied, or alternating current may be used to run a D. C. generator (which is preferably portable), or an alternating current generator may be used with a rectifier. Storage batteries or other sources of direct current may, of course, be used. While we prefer to use direct current, it is possible to produce a coating by the use of alternating current. The coating apparently starts to form when the alternating current is passing in such direction that the copper is the anode, while the coating acts as a one-way valve on account of its rectifying properties.

A slightly oxidized or sulphidized surface of tarnished copper requires no cleaning prior to the production of patina thereon by our method. Those that are somewhat dirty may be cleaned by first making a light application of the patina, (the solution acting as an "electrolytic cleaner") and washing and scrubbing off any of the coating that can be dislodged, leaving the surface either as a clean metallic surface or one coated with adherent patina, and then applying a second, heavier coat of patina. However, if the copper is very dirty and black, it should be cleaned before the process is put in operation as by swabbing it with an ordinary sulphuric acid "pickle" and then washing off the acid. If the patina is applied over very dirty copper, blackened by long exposure and not cleaned, the patina will appear as well as when applied over clean copper, but will not adhere permanently.

In the application of the coating by our method to roofs or other objects of a fixed nature, few special precautions are needed and the ordinary

workman can be readily taught to apply it. The swab or roller should not be kept in one position too long. Otherwise, heating will ensue from the action of the current and the deposit will be black, instead of being green with a blue tinge. Such a black deposit can be removed and the spot then covered by a second proper application of the swab or roller.

In producing the patina on copper roofing, it is preferable to ship the uncoated copper, cut it on the ground to the size to be used on the roof, lay it on a flat surface, coat it by the roller method, and then raise it to the roof and lay as usual, though as already made apparent, the method can be readily applied to copper in place on the roof. The patina is readily removed by the usual soldering fluxes so that the coating does not interfere with making soldered joints.

While the swab or roller form of our method lends itself readily to the much needed operation of rapidly producing patina on fixed articles, the method is also applicable to the formation of patina on objects of copper or copper alloy, such as sheet, spandrels and the like, in the factory before shipment for erection or use. In such cases, the coating may be applied either by the swab, roller or similar methods, or by electrolysis in vats.

If sheets are to be treated in a vat by our method, one side of each sheet could be readily protected from the treatment. This could be effected either by stopping-off the back or by facing two sheets together so that their surfaces in contact would not be coated. If desired, however, both sides of a single sheet can be readily coated.

Coatings of various thicknesses produced by our method will stand considerable flexing or distortion of the underlying copper without peeling or flaking off in pieces. This is probably due to the fact that our method permits the production of a satisfactory color without the necessity of producing a very thick coating. In other words, the coating produced by our method has, what would be termed in speaking of paint pigments, a good "covering power". This is quite an advantage, since the thinner the coating, the less likelihood there will be of a flaking off as a result of bending or expansion and contraction of the underlying metals.

Coatings about 0.0005'' thick or less, upon copper sheets, give a satisfactory appearance, and those 0.0025'' or thicker have been made which showed extremely good adherence even though the copper sheet was severely bent. There is thus a considerable tolerance in the thickness to which the patina may be built up without adversely affecting looks or adherence. The coating is formed in close contact with the metal, from the copper ions produced right at the surface by the anodic attack, and it remains integrally connected to the metal. Copper objects coated with our patina may be shipped without the coating flaking off in shipment.

Copper sheets having patina formed in accordance with our invention have withstood rain, frost, snow and severe weather temperature changes without appreciable peeling, flaking or excessive powdering. Copper plates so coated have been exposed to changes in temperature from −40° F. to +140° F. for several cycles, both dry, and wet so that ice would form on the coating, without damage. The coating has been exposed to moist hydrogen sulphide gas and to moist sulphur dioxide, and did not blacken. Insofar as we can determine by observation of roofs so coated, and by laboratory tests, the coating is permanent and adherent, provided the copper is initially clean, or, if very dirty, has been properly cleaned. It may be possible to rub off as a powder some of the upper part of a thick layer, but the lower part adheres tenaciously to the metal.

When the initial color is made a blue-green by use of suitable current density and time, we find a slight trend toward a more truly green color on exposure. Moist sulphur dioxide gas turns the carbonate patina greener in the same way, as does a short dip in SO_2 solution. Neither treatment causes flaking of the coating, though CO_2 is given off. The reaction might be written

$$2(CuCO_3.Cu(OH)_2) + H_2O + SO_2 =$$
(Malachite)
$$CuSO_4.3Cu(OH)_2 + 2CO_2$$
(Brochantite)

Long soaking in SO_2 solution will change the coating to a reddish color, the sulphite apparently being formed. Under conditions such that SO_2 can be catalyzed to SO_3 it appears that moist weak SO_2, as present in industrial atmospheres, will in a short time (compared to that required for formation of natural patina) change the basic carbonate to the basic sulphate, without causing a flaking of the patina.

The basic carbonate (malachite) and the basic sulphate (brochantite) are isomorphous, i. e. crystallize alike. To this fact is probably due the ability of the coating to change its composition to that of natural, slowly-formed patina, without dimensional changes that would cause flaking.

That the basic carbonate coating changes rather rapidly to the basic sulphate is shown by the fact that a coating of the carbonate applied to a clean sheet of copper by the roller method the first part of March and exposed on the roof of a building in Columbus, Ohio, was analyzed about three months later and found to be already three-quarters transformed to basic sulphate without noticeably changing its color or losing its adherence. The uncoated copper roof on which this sample was exposed was itself still in the dirty black stage without sign of patina after five years. In atmospheres carrying sulphur gases from the combustion of fuel, the carbonate patina therefore serves as an intermediate product, of the desired color and adherence, which changes automatically to the natural patina.

The color of the initial patina produced by the application of our method to copper has been compared with many copper roofs bearing natural patina. It has been found to be a very good match and, in fact, better than the more vivid blues and greens on the one hand and the whiter colors on the other, obtained by those various processes of the prior art which attempt initially to produce an insoluble basic copper sulphate upon the copper or copper alloy. Furthermore, the method used by us is much more simple and is effective to produce an adherent patina of the desired color in a much shorter period of time at a markedly lower cost. In addition, that phase of our method which makes possible the production of the patina directly upon the copper or copper alloy without immersing it in a bath is markedly advantageous from a practical standpoint.

As indicated, our invention is also applicable to copper alloys as well as to pure copper. Thus, it has already been successfully applied to such

alloys as brasses with as much as 40% zinc, aluminum bronze, tin bronzes, "Tempalloy" and "Everdur". The only copper alloy we have yet tried on which the present method does not produce a good coating is an alloy of 80% copper and 20% nickel. One containing 10% nickel was slow in taking the coating, but with a 15 minute treatment it took a good coating. Thus, the advantages of the greater strength of these alloys over that of copper may be combined with that of the attractive patina.

Having thus described our invention, what we claim is:

1. The method of producing an artificial patina on copper or its alloys which comprises applying thereto an electrolyte embodying an 8% concentration of sodium bicarbonate, and then subjecting such electrolyte to electrolysis with the copper or copper alloy forming the anode by passing therethrough an electrical current at a current density of 18 amps/dm² for approximately 1 minute.

2. The method of producing an artificial adherent patina on copper or its alloys which comprises applying thereto an electrolyte embodying a strongly basic solution of readily soluble carbonates selected from the group comprising carbonates of the alkali metals and of ammonium, bicarbonates of the alkali metals and of ammonium, and then subjecting such electrolyte to electrolysis with the copper or copper alloy forming the anode.

3. The method of producing an artificial adherent patina on copper or its alloys which comprises applying thereto an electrolyte embodying a strongly basic solution of readily soluble carbonates selected from the group comprising carbonates of the alkali metals and of ammonium, bicarbonates of the alkali metals and of ammonium, and then passing a current of high current density through the electrolyte to effect electrolysis with the copper or copper alloy forming the anode.

4. The method of producing an artificial adherent patina on copper or its alloys which comprises applying thereto an electrolyte embodying a 2% to 10% concentration of sodium bicarbonate, and then subjecting such electrolyte to electrolysis with the copper or copper alloy forming the anode by passing therethrough an electrical current at a current density ranging from 1 amp/dm² to 20 amps/dm².

5. An artificially produced adherent patina on copper or its alloys produced by the method of claim 3.

CLARENCE E. IRION.
GEORGE L. CRAIG.