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PRODUCT FOR EFFECTING A COLD CHEMICAL OXIDATION OF COPPER AND ITS ALLOYS

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My invention relates to a product and method for blackening or effecting a cold chemical oxidation of brass and/or copper and their alloys.

An object of my invention is to provide a novel and improved method of cold treating brass and/or copper and their alloys to blacken the surface thereof.

Another object of my invention is to provide a novel solution which may be easily applied to brass and/or copper and their alloys to blacken the surface thereof.

My invention has particular application in blackening the front edge or character face of Linotype matrices; wherein, the character face of a matrix may be blackened by my invention more easily and more simply than by any other method or means now known. It is clear, however, that my invention, hereinafter specifically disclosed, will have other uses and applications than that specifically mentioned.

In accordance with my invention, I preferably form a solution consisting of a cupric salt, selenium or tellurium, a catalyst comprising arsenic trioxide, hydrochloride acid, an alcohol, alkylaryl sulfate known commercially as "aerosol" and water.

With respect to the chemicals in the solution product aforementioned, the selenium or tellurium acts as a blackening agent for the copper, which is in solution as a copper salt. Although cupric chloride may be used, preferably I have used cupric sulfate, which is cheaper than cupric chloride, and yet which is completely compatible with the metallic surfaces to be treated, that is brass and/or copper and their alloys. The selenium or tellurium may be in solution as one of the oxygen acids thereof, that is selenous or selenic acid, or tellurous or telluric acid; or in solution as a water soluble salt which may be thought of as derived from the aforementioned oxygen acids, for example, sodium or potassium tellurite. The cupric sulfate, in solution with selenous or selenic acid, or with tellurous or telluric acid, or with any of the water soluble salts of these acids, provides in solution either copper selenite, copper selenate, copper tellurite or copper tellurate, depending upon the extent of oxidation of the selenium or tellurium in solution. Copper selenite and copper tellurite are generally readily oxidized to the selenate and tellurate, respectively; and although this may occur to some extent in the solution, it at least occurs upon oxidation of the coated metallic surface. Therefore, it can generally be considered that the solution comprises either copper selenate or copper tellurate, even though as aforementioned, the copper selenium or tellurium may be in solution, at least in part, as copper selenite or copper tellurite.

In essence, it is a purpose of my invention to maintain the copper selenate or copper tellurate in solution until brought in contact with the metallic surface to be coated, and then to controllably effect the precipitation or plating of the copper selenate or copper tellurate onto the metallic surface.

Copper selenate or copper tellurate is generally insoluble in water; however, I have found that by maintaining

the solution acidic the copper selenate or copper tellurate will remain in solution. For this, I provide in my novel solution product, preferably, the readily available hydrochloric acid which acts as an electrolytic agent for maintaining the copper selenate or copper tellurate in solution as aforementioned. Any of the stronger acids might be used for this purpose, in addition to hydrochloric acid; but since it is preferable to have chloride in the solution, as will be subsequently mentioned, I generally use hydrochloric acid.

The alcohol and alkylaryl sulfate components of my novel and improved solution act to control the plating of the copper selenate or copper tellurate onto the metallic surface. First, with respect to the alcohol in solution, I have found that either isopropyl or methanol is to be preferred; however, in view of the fact that other alcohols might prove just as acceptable, I do not intend the scope of my invention to be limited to isopropyl alcohol and methanol. The only specific requirement is that the alcohol be compatible with the other elements in solution so that it will not effect a precipitation of any of the components of my solution. As between isopropyl alcohol and methanol, I have found that the former is to be preferred because it will hydrolize to aid in maintaining the solution acidic. That is, the isopropyl alcohol in the acidic solution results in an inter-action between the acid and alcohol in solution which produces an ester and which will hydrolize. The alcohol and the alkylaryl sulfate, aerosol, act as suppressors or retarders; in other words, they slow down the plating process to produce a finer grain of surface or a smoother finish. The type of finish desired may be variable depending upon the percentage of alcohol and aerosol in relation to the amount of water, even to the extent that these controlling components may be omitted entirely.

As to a catalyst, I have found that arsenic trioxide effects a fast precipitation of the copper selenate or copper tellurate and further acts to impart a blacker surface than if any other type of suitable catalyst, now known, were used. It is indeed conceivable, however, that some catalyst equivalent in action to arsenic trioxide, with respect to its effect as a catalyst in my novel solution, may be subsequently found; and I intend that such equivalent catalyst should be within the broad scope of my invention. I believe that a cyanide catalyst would be effective in my solution, but would be unsatisfactory because the cyanides would be generally too dangerous to use together with the acid in solution.

A specific formulation of my novel and improved solution is as follows: For each batch of solution, I have used an amount of water which may vary between 22 and 54 gallons depending upon the dilution of solution desired. For transporting my solution product, it is, of course, desirable to have a highly concentrated solution which may then be diluted as desired by the user. In this regard, it is believed that less than 22 gallons of water may be used; a super-saturated solution would be formed using only the minimum requisite of water necessary to receive the cupric sulfate, arsenic trioxide and selenium or tellurium in solution. Next, the selenium or tellurium, cupric sulfate, and arsenic trioxide are put into the water.

In each batch of solution, I have preferably used proportionately between three and twelve pounds of cupric sulfate, between three and twelve pounds of selenium or tellurium, and between two and six pounds of arsenic trioxide. With respect to the selenium or tellurium, I preferably have used, in each batch of solution, selenium dioxide, in an amount approximately equal by weight to the amount of cupric sulfate. Next, I add the hydrochloric acid in an amount approximately equal to 110 to 170 fluid ounces. Next, I add from between two to four

pounds of aklylaryl sulfate. Last, the alcohol is added in an amount between five and twenty gallons. As previously mentioned, the amount of alcohol may be varied to control the speed of the plating action. It should also be particularly noted that in forming a highly concentrated solution, which would be easily transportable, the alcohol may be omitted from the solution and added by the user according to instructions.

It should be noted that with respect to the amount of copper in relation to the amount of selenium or tellurium, that one can generally use from between 15% more copper to 15% less copper than the selenium or tellurium. Generally, it is preferable to include in solution more selenium or tellurium than copper because some of the copper blackening agent will react with the surface to be treated.

In using tellurium instead of selenium in my solution the tellurium dioxide is unsoluble in water; and a sodium or potassium tellurite can be used. Preferably, I dissolve the tellurium metal itself in hydrochloric acid beefed up with hydrogen peroxide to form telluric acid. In this respect I have used three-fourths of a fluid ounce of hydrochloric acid, one ounce of hydrogen peroxide and one ounce of tellurium to form approximately 1½ ounces of telluric acid. In every batch of solution product, I would use from three to twelve pounds of telluric acid in place of the selenium dioxide. It should also be noted that, instead of using selenium dioxide, the selenium metal itself can be dissolved in hydrochloric acid, as with respect to the tellurium, to form the selenous or selenic acid.

A plating or precipitation of blackened copper, copper selenate or copper tellurate, onto the surface to be treated, brass and/or copper and their alloys, is effected by immersing, spraying or brushing the article to be treated with my novel solution product, which produces the desired blue-black or jet-black finish. There is actually a chemical reaction or inter-action between the metallic surface to be treated, and the solution product, so that the blackened copper precipitate is absorbed in and becomes a part of the surface treated; therefore, it is more than a mere coating. After coating, within twenty-four hours, the surface is oxidized and hardened. In this respect, I have found that with chloride in solution, some copper chloride is formed which acts as a surface hardener. It might be desirable to maintain a softer surface, and in which case, the chloride might be left out of the solution. The alkylaryl sulfate, in solution, not only acts as a plating control agent, but also acts as a spreading agent for the solution and as a detergent for penetrating any film of oil which might be retained on the surface to be plated.

My invention has been practiced, as heretofore disclosed, and has been found to accomplish all of the aforementioned objectives and advantages. It will be obvious to those skilled in the art that my invention may be modified in many respects without departing from the essence of my invention; and therefore, I intend to be limited solely by the scope of the appended claims.

What I claim is:

1. A solution batch consisting of in proportion approximately 3 to 12 pounds of a copper blackening agent selected from the group consisting of oxygen acids and salts of selenium and tellurium, a copper salt in an amount by weight approximately equal plus or minus 15% to the weight of copper blackening agent, approximately 2 to 6 pounds of arsenic trioxide, approximately 110 to 170 fluid ounces of hydrochloric acid, approximately 2 to 4 pounds of alkylaryl sulfate, approximately 5 to 20 gallons of an alcohol, and approximately 22 to 54 gallons of water.

2. A solution batch consisting of in proportion approximately 3 to 12 pounds of selenium dioxide, a cupric salt in an amount by weight approximately equal plus or minus 15% to the weight of the selenium dioxide, approximately 2 to 6 pounds arsenic trioxide, approximately 110 to 170 fluid ounces of hydrochloric acid, approximately 2 to 4 pounds of alkylaryl sulfate, approximately 5 to 20 gallons of an alcohol selected from the group consisting of isopropyl alcohol and methanol, and approximately 22 to 54 gallons of water.

3. A solution for coating copper and its alloys consisting essentially in proportion of about 3–12 pounds of a copper blackening agent selected from the group consisting of oxygen acids and salts of selenium and tellurium, a copper salt in an amount by weight approximately equal to plus or minus 15% of the weight of copper blackening agent, sufficient arsenic trioxide to catalyze the solution's action on the surface to be coated, a strong acid in an amount sufficient to maintain the copper blackening agent in solution, and solvent in an amount between about 20 and 75 gallons including water.

4. A solution for coating copper and its alloys consisting essentially of in proportion about 3–12 pounds of selenium dioxide, a cupric salt in an amount by weight approximately equal plus or minus 15% to the weight of the selenium dioxide, sufficient arsenic trioxide to catalyze the solution's action on the surface to be coated, hydrochloric acid in an amount sufficient to maintain the copper blackening agent in solution, about 2 to 4 pounds of alkylarylsulfate, and solvent in an amount between about 20 and 75 gallons including water and an alcohol selected from the group consisting of isopropyl alcohol and methanol in a proportionate amount of between 5 and 20 gallons.

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