This invention relates to the coloring of copper and copper alloy surfaces.

It is frequently desirable in the finishing of articles such as metal buttons and buckles, costume and cosmetic accessories, lamp bases and stands, urns, screens, tacks, particularly upholstery tacks, builder's hardware and architectural items, and the like, fabricated from copper and copper alloys, such as brass, to treat the surfaces of the article to impart thereto a color not characteristic of the untreated metal. Various shades of brown including tan, greenish-brown, brownish-gold, etc., are considered particularly desirable.

In accordance with the present invention, I produce these and other colors on copper and copper alloy surfaces by a process which comprises contacting the surface with an aqueous solution containing an alkali or alkaline earth metal chlorite, e.g., sodium, potassium, and calcium chlorides, and an alkaline salt. The alkali and alkaline earth metal chlorites are salts of chlorous acid and when chemically pure are essentially neutral in reaction. In the preferred mode of executing the process the surface to be colored is immersed in the salt solution.

Among the many alkaline salts which may be employed in the process of my invention may be mentioned: sodium carbonate, sodium metasilicate, sodium tetraborate, trisodium phosphate, tetrasodium pyrophosphate, sodium sesquisilicate, sodium orthosilicate, and the corresponding potassium and alkaline earth compounds where they are water-soluble. If desired, the process may be executed using a plurality of alkaline salts and/or chlorites. The presence of substantial amounts of a strong alkali such as sodium or potassium hydroxide in the coloring solution is without harmful effect, in fact may be advantageous particularly where it is desired to accomplish the coloring as rapidly as possible or to impart colors other than shades of brown, for example, a bluish, purplish, or greenish color.

It will be understood that the words "color" and "colored" herein and in the appended claims in the strict sense and do not include black or blackening.

The exact color produced on the surface treated depends upon various factors including the composition of the surface, the particular salts being employed, the concentration of the salts, the temperature at which the solution is maintained, and the contact or treating time. The conditions necessary to achieve a particular color can be readily determined by simple experiments well within the skill of those experienced in the metal coloring art.

I have found that in most cases the solution with proper adjustment of other conditions may be effectively operated at any temperature between 70° F. and its boiling point. However, I prefer to operate the solution at temperatures between 120° F. and 200° F.

The ratio of chlorite to alkaline salt in the solution may vary within fairly wide limits, but I prefer to prepare the solution so that it contains the chlorite and alkaline salt in a ratio by weight within the range 1:1 to 1:2.5. Using such ratios of chlorite and alkaline salts, I have been able in many cases to obtain equivalent results from saturated solutions and solutions containing as little as a total of 4 grams per liter of the salts. The less concentrated solutions, however, must usually be operated at a higher temperature in order to accomplish the coloring in the same length of time. In operating at high concentrations, I have noticed that no adverse effect results from the presence of substantial amounts of undissolved salts in the solution. In general, I prefer to employ a solution in which the concentrations of the salts are within the following limits: chlorite-10 g./l., alkaline salt-20 g./l. to chlorite 80 g./l., alkaline salt-160 g./l. I usually employ sodium chlorite in the practice of the invention because of its solubility and because it is readily available commercially.

Some combinations of the salts used in the execution of the invention give various colors while other combinations appear capable of imparting only a relatively few colors or of giving only a single color. I have found that the solution as prepared with sodium chlorite and either sodium carbonate or trisodium phosphate will give the greatest number of colors of the various chlorite-alkaline salt mixtures. When prepared with borax or sodium metasilicate in lieu of sodium carbonate or trisodium phosphate, the solution is relatively limited in coloring range. A very attractive brownish-gold color may be achieved, however, with a solution containing about 66 grams per liter of borax and an equal amount of sodium chlorite. This solution is best operated at the boiling point. If sodium metasilicate is used instead of borax, a greenish to brown color results depending upon the temperature of operation and the length of the treating period. I prefer to carry out my process in a container formed of low carbon steel. The container or tank should be welded, not soldered.
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Because the solution will quickly dissolve solder,enameled ware and ceramic vessels are not recommended for use with solutions which also contain caustic because such solutions will gradually attack the enamel or ceramic and frequently the solution may be poisoned by components of the enamel.

In making up the solution, the tank is usually filled about three-quarters full of water after which the pre-mixed salts are added with stirring until they are completely dissolved. The tank is then filled to the operating level with additional water.

I have found that unlike pure chlorite a mixture of a chlorite and an alkaline salt containing from 1 to 2.5 parts of the alkaline salt for each 1 part of chlorite is not explosive upon percussion, the presence of organic matter and does not readily increase the inflammability of ordinary brics when permitted to remain in contact therewith. Also, the mixture or composition is as reactive with sulfur and when brought into contact with acid is less prone to give off dangerous amounts of chlorine dioxide. This last characteristic of my composition is particularly desirable from the standpoint of safety since many metal surface treatments involve the use of acid solutions which are sometimes rather carelessly handled. Thus, when accidentally spilled about plating room in which acid solutions are being used, my composition does not involve the risk of chlorine dioxide liberation that would be involved if the chlorite handled separately were so spilled.

Consider the composition resulting from intimately mixing an alkali or alkaline earth metal chlorite with an alkaline salt a part of my invention. Where it is desired to practice the process of a highly alkaline solution, the composition may include substantial amounts, i.e., up to 50%, sodium or potassium hydroxide.

In commercial practice the composition containing 2 parts alkaline salt per part chlorite is used to water to form the coloring solution in a proportion of about 1 lb. for each gallon of water.

During the coloring operation, water should be filtered before it is replaced that lost by operation; otherwise, the solution may become concentrated. No precise analytical control of the solution is required. The need for more is indicated by a slowing up of the coloring e.g., when the coloring rate has dropped about 15%. I usually add about 4 ounces of the original pure for each gallon of water present in the tank.

Consider it highly important to thoroughly clean the copper or copper alloy surface. Clean can be done with alkaline cleaners, vapor or sorbent de-greasers, or by emulsion cleaning. The cleaning is not as critical as that for brightening, but it is recommended to the end of insuring uniform coloring that the surface be to the extent that water when placed on surface remains thereon as a continuous film at least one minute without separating into droplets, i.e., no "water-break."

If the case of highly buffed surfaces, it is excellently desirable to clean the surface to no "water-break." However, the work is preferably roughened by rinsing after cleaning and then dipped in sodium cyanide solution as in the instance of galvanically deposited copper.

I have found that I can usually produce the red color on pure copper and high copper alloys in from 1 to 10 minutes. In some cases less than 30 seconds is sufficient. Low copper alloys may require as long as 20 minutes. After coloring, the work should be thoroughly rinsed in running cold water and then in hot water if it is to be dried.

In the immersion treatment, small parts can be supported in steel baskets or cylinders, and large objects on steel or iron racks, hooks, or pipes. Where baskets are used, it is advisable to shake the work occasionally so that all surfaces will be exposed to the solution.

Following the coloring operation, the work may be subject to various after-treatments such as tumbling in sawdust, corn cob drying meal, or paraffin coated ground cork. Where the work must withstand severe outdoor weathering, it is advisable to augment the protective effect of the finish with either lacquer, oil, or wax.

The herein described process is suitable for coloring all copper alloys containing as little as 60% of copper. Thus 60:40, 65:35, 70:30, 80:20, and 90:10 brasses are readily colored, as well as tin bronzes, silicon bronzes, beryllium copper, and phosphor bronzes. Pure copper whether cast, rolled, or electroplated, is quickly given a deep finish. The process is also applicable to the coloring of electrolytically deposited brass alloys where the nominal copper content of the alloy is 60% or more.

I claim:

1. A solid composition in finely divided form adapted for use in aqueous solution to color copper surfaces or surfaces of copper alloys containing not less than 60% copper which consists of about 1 part by weight of an alkali metal chlorite from about 1 to about 2.5 parts by weight of an alkaline salt having an alkalinity equal to or greater than that of tetrasodium pyrophosphate but less than that of caustic soda or potash.

2. A solid composition in finely divided form adapted for use in aqueous solution to color copper surfaces or surfaces of copper alloys comprising not less than 60% copper which consists of about 1 part by weight of sodium chlorite and about 2 parts by weight of an alkaline salt having an alkalinity equal to or greater than that of tetrasodium pyrophosphate but less than that of caustic soda or potash.

3. A process for coloring copper surfaces and surfaces of copper alloys containing not less than 60% copper which comprises contacting the surface with an aqueous solution consisting essentially of water, a chlorite of the group consisting of alkali and alkaline earth metal chlorites, an alkaline salt having an alkalinity equal to, or greater than, that of tetrasodium pyrophosphate but less than that of caustic soda or caustic potash, in proportions by weight within the range of 1 to 2.5 parts of the alkaline salt per part of the chlorite, and 0 to 50%, based on the total weight of the chlorite and alkaline salt, of a caustic alkali, the concentration of the salts in the solution being within the range of 4 grams per liter to saturation.

4. A process for coloring copper surfaces and surfaces of copper alloys containing not less than 60% copper which comprises immersing the surface in an aqueous solution consisting essentially of water, an alkali metal salt of chlorous acid, an alkaline salt having an alkalinity equal to, or greater than, that of tetrasodium pyrophosphate but less than that of caustic soda or caustic potash, in proportions by weight within the range of 1 to 2.5 parts of the alkaline salt per part of
the chlorite, the concentration of the salts in the solution being within the range of 4 grams per liter to saturation.

5. A process for coloring copper surfaces and surfaces of copper alloys containing not less than 60% copper which comprises immersing the surface in a hot aqueous solution consisting essentially of water, sodium chlorite and an alkaline salt having an alkalinity equal to, or greater than, that of tetrasodium pyrophosphate but less than that of caustic soda or caustic potash, in proportions by weight of about 1 to 2, the concentration of the chlorite in the solution being within the range of 10 grams per liter to 80 grams per liter.

6. A solid composition in finely divided form adapted for use in aqueous solutions to color copper surfaces and surfaces of copper alloys containing not less than 60% copper, the composition consisting essentially of a chlorite of the group consisting of the alkali and alkaline earth metal chlorites, an alkaline salt having an alkalinity equal to, or greater than, that of tetrasodium pyrophosphate, but less than that of caustic soda or caustic potash, in proportions by weight within the range of 1 to 2.5 parts of the alkaline salt per part of the chlorite, and 0 to 50% based on the total weight of the chlorite and alkaline salt of a caustic alkali.

7. A solid composition in finely divided form for use in aqueous solution to color copper surfaces or surfaces of copper alloys containing not less than 60% copper, the composition consisting essentially of an alkali metal chloride, an alkali salt having an alkalinity equal to, or greater than, that of tetrasodium pyrophosphate but less than that of caustic soda or caustic potash, in proportions by weight within the range of 1 to 2.5 parts of the alkaline salt per part of the chlorite, and 0 to 50% based on the total weight of the chlorite and alkaline salt of a caustic alkali.

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