This invention relates to a process for blackening copper and copper alloys and has for its object the attainment of highly successful results in producing a black coating on such metal parts without the disadvantages attendant upon the use of baths heretofore used for this purpose.

Up to the present time, the art of blackening copper and copper alloys has been confined for the most part to processes which give an oxide or sulphide film on the surface. While the baths to produce the black sulphide films are comparatively simple and easy to operate, non-toxic and free from explosion and fire hazard, the film is, however, rather soft, and its adhesion to the metal surface is poor. Moreover, the sulphide film can only be produced satisfactorily on copper or alloys very high in copper. Other copper alloys would need to be copper plated before blackening. A protective coating of lacquer or wax is necessary to preserve the sulphide film and insure its permanence.

Black copper oxide films have been produced on copper and copper alloys by a number of methods. This black oxide is a durable coating and adheres tenaciously to the base metal. The black oxide film, moreover, can be produced in either a dull or shiny finish. However, the baths formerly used to produce the black copper oxide coatings have had many disadvantages. One commonly used bath compound of copper carbonate and ammonium hydroxide is difficult to operate because of the sensitivity of the bath to deficiencies or excesses of ammonium hydroxide. The bath also has a short life and must be discarded when used for only a short time.

Another type of bath composed of caustic soda and sodium chlorite produces a satisfactory black copper oxide coating, but has the disadvantage of being composed partly of a hazardous substance—sodium chlorite. This material is especially hazardous in the dry state as it is a powerful oxidizing agent. Wood, cloth, paper and other common packaging materials are rendered highly inflammable by the sodium hydroxide-sodium chlorite mixture.

I have discovered that a bath comprising a water solution of a water soluble salt of an aryl sulphone monochloramide made alkaline with a strong water soluble alkali is free of the objections above mentioned and is effective for use in the blackening of copper and copper alloys.

Of the aryl sulphone monochloramides, I have found those having benzene or one of its homologues as part of the molecule, to be especially suitable for use in a copper blackening bath. One compound of this group particularly suitable from the standpoint of commercial use, is the sodium salt of benzensulphonemonochloramide. This organic compound is not hazardous from the standpoint of fires and explosion in either the dry state or in solution. Baths for blackening copper employing this material can vary widely in proportion, yet give a suitable black. As little as ½% by weight of the sulphone monochloramide and ½% of water soluble alkali give excellent blackening baths. Large amounts also produce satisfactory baths and the amounts are limited by the solubilities of the components. However, there is no advantage in the use of higher concentrations and because of economic reasons I prefer the more dilute solutions.

Among the strong water soluble alkalies acceptable for this composition are those of the alkali metal and alkali earth metal groups. While the carbonates of some of these are satisfactory, the alkali metal hydroxides appear to be most suitable.

Of the copper alloys tested with this bath, I have found those containing zinc, lead, tin, phosphorus, silver, aluminum, silicon and beryllium to give unusually good black coatings. I do not limit myself, however, to the alloys mentioned above, and this list is given to show the wide range of alloys which may be blackened by my process.

Henceforth are given by way of example several specific disclosures of my process for the black coating of copper and two of its principal alloys.

**Example No. 1.—For copper**

Two parts by weight of the sodium salt of benzensulphonemonochloramide and two parts by weight of sodium hydroxide are dissolved in 100 parts by weight of water. This solution is heated to a temperature of 180° F. and the piece of copper to be coated previously cleaned by the customary mechanical and chemical methods is immersed in the bath for a period of from 5 to 15 minutes. Upon removing the copper piece from the bath, it is rinsed in water for a sufficient length of time to remove completely any residue from the alkaline bath and is then dried. A durable, velvety, jet black coating which adheres tenaciously to the copper piece will be present on its surface. This coating can be made shiny by gentle buffing or by means of oil or wax finishes.
Example No. 2.—For brass (85% copper, 15% zinc)

Two parts by weight of the sodium salt of toluenesulphonemonochloramide and two parts by weight of potassium hydroxide are dissolved in 100 parts by weight of water. This solution is heated to boiling, and the piece of brass to be coated, previously cleaned by the customary mechanical and chemical methods is immersed in the bath for a period of from 5 to 15 minutes. Upon removing the brass piece from the bath, it is rinsed in water for a sufficient length of time to remove completely any residue from the alkaline bath and is then dried. A durable, velvety, jet-black coating which adheres tenaciously to the brass piece will be present on its surface. This coating can be made shiny by gentle buffing or by means of oil or wax finishes.

Example No. 3.—For beryllium copper

Two parts by weight of the sodium salt of benzene sulphone monochloramide and four parts by weight of sodium carbonate are dissolved in 100 parts by weight of water. This solution is heated to a temperature of 200° F. and a piece of beryllium copper to be coated, previously cleaned by the customary mechanical and chemical methods is immersed in the bath for a period of from 5 to 15 minutes. Upon removing the piece from the bath, it is rinsed in water for a sufficient length of time to remove completely any residue from the alkaline bath and is then dried. A durable, velvety, jet-black coating which adheres tenaciously to the piece will be present on its surface. This coating can be made shiny by gentle buffing or by means of oil or wax finishes.

It is to be understood that the organic sulphone monochloramides given in the above examples are not confined to the examples cited but may be interchanged. Moreover, other organic sulphone monochloramides of this type may be substituted. In like manner the alkalies used may be interchanged.

The temperature of the bath for the blackening operation is not limited to those given in the examples. The temperature may vary widely and the rate of blackening will be relatively low at the lower temperatures and high at the higher temperatures. I have found that temperatures as low as 125° F. will produce a satisfactory black, but is time consuming. Temperature between 175° F. and boiling will be found to be most suitable for blackening baths.

What I claim is:

1. The process of blackening copper and its alloys in which the metal is immersed in a solution consisting of 2 parts of the sodium salt of benzene sulphone monochloramide, 2 parts of sodium hydroxide and 100 parts of water, said solution being heated to a temperature between 175° F. and boiling, and the metal held in said solution for a sufficient time to produce the desired depth of color.

2. The process of blackening copper and its alloys in which the metal is immersed in a solution consisting of a water solution of a water soluble salt of an aryl sulphone monochloramide made alkaline with a strong water soluble fixed alkali, said solution being heated to a temperature between 175° F. and boiling and the metal held in said solution for a sufficient time to produce the desired depth of black.

3. The process of claim 2 in which the proportion of aryl sulphone monochloramide to the strong water soluble fixed alkali is 1:1.

4. The process of blackening copper and its alloys in which the metal is immersed in a solution consisting of a water solution of a water soluble salt of an aryl sulphone monochloramide made alkaline with a strong water soluble fixed alkali, said solution being heated to a temperature between 175° F. and boiling and the metal held in said solution for a sufficient time to produce the desired depth of black.

5. The process of blackening copper and its alloys in which the metal is immersed in a solution consisting of a water solution of the sodium salt of benzene sulphone monochloramide made alkaline with a strong water soluble fixed alkali, said solution being heated to a temperature between 175° F. and boiling and the metal held in said solution for a sufficient time to produce the desired depth of black.

6. The process of blackening copper and its alloys in which the metal is immersed in a solution consisting of a water solution of the sodium salt of toluenesulphonemonochloramide made alkaline with a strong water soluble fixed alkali, said solution being heated to a temperature between 175° F. and boiling and the metal held in said solution for a sufficient time to produce the desired depth of black.

7. The process of blackening copper and its alloys in which the metal is immersed in a solution consisting of a water solution of a water soluble salt of an aryl sulphone monochloramide made alkaline with an alkali metal hydroxide, said solution being heated to a temperature between 175° F. and boiling and the metal held in said solution for a sufficient time to produce the desired depth of black.

8. The process of claim 6 in which the proportion of organic sulphone monochloramide to alkali metal hydroxide is 1:1 and the solution strength is 4 parts by weight of said compounds to 100 parts by weight of water.

9. The process of blackening copper and its alloys in which the metal is immersed in a solution consisting of a water solution of a water soluble salt of an aryl sulphone monochloramide made alkaline with an alkali metal carbonate, said solution being heated to a temperature between 175° F. and boiling and the metal held in said solution for a sufficient time to produce the desired depth of black.

ISAAC LAIRD NEWELL.

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