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COLORING OF BRONZE POWDERS

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This invention relates to manufacture of bronze powders and it comprises a process of making bronze powders of various gold shades from aluminum bronze powders by dyeing the same with suitable dyes or mixtures thereof, the process also usually including mordanting and fixing operations; and it further comprises the aluminum bronze powders produced by the said process, these powders comprising finely flaked aluminum mordanted, fixed and dyed in various non-tarnishing golden shades; all as more fully hereinafter set forth and as claimed.

The so-called gold bronze powders of commerce have heretofore been produced by flaking copper or copper alloys. Alloys of copper with zinc have geen most commonly employed. The proportion of zinc used in these bronze powders has varied considerably according to the shade of gold desired. A common bronze powder of the so-called pale gold shade is produced from an alloy containing up to 20 per cent zinc. The so-called rich gold shade is made from an alloy containing 12 per cent zinc, etc.

While bronze powders from copper-zinc alloys are almost exclusively used they have several well-recognized disadvantages. The most important of these disadvantages is the tarnishing and discoloring of these bronze powders. These powders also possess the disadvantage of flaking off, to which there is a great deal of objection when used on food wrappers and containers. In order to partly overcome these objectionable characteristics, the lithographers and label printers have been obliged in many cases to give their finished work a coating of varnish.

It has also been proposed to dye aluminum bronze powders with various dyes to produce a large variety of colors. While powders produced in this fashion are doubtless non-tarnishing, they have not yet been adopted to any important extent due largely to the fact that they are not light-fast.

It has now been found that gold bronze powders of various light-fast shades can be produced from aluminum bronze powders by simple dyeing operations in which use is made of mordanting and fixing operations. Gold shades ranging from light to dark or from apple green to rich gold can be readily produced by the operations subsequently to be described. The new powders present brilliant and attractive shades. They have a greater covering and spreading power per pound than the powders made from copper alloys. Moreover they are non-tarnishing. They do not have the same tendency to flake off as that shown by the copper alloy powders. They are non-bleeding in nature.

In the present process an aluminum bronze powder is prepared by the customary hammering operations which form no part of the present invention. Prior to the polishing operation such a bronze powder is advantageously cleaned to remove any greasy substance from the surface of the flakes. This can be accomplished by use of the usual cleaning solutions employed in the electroplating art or organic solvents can be employed.

After cleaning, the powder may be subjected to the dyeing operation. A mordant can be employed in the dye bath or the powder can be previously mordanted. But prior to dyeing it is advantageous to coat the surface of the particles with a film of aluminum oxide. This can be accomplished by the use of a dilute boiling soda solution, say 2 to 5 per cent for example, or various dilute organic acids such as oxalic, citric, lactic or tannic acids can be employed. If a dilute alkaline solution, such as an alkali metal phosphate solution is employed, it is possible to combine the cleaning and oxidizing procedures in one step.

While the oxidizing of the flaked aluminum by the methods described is not essential in the process of the present invention it is highly advantageous. When this oxidizing step is used the mordanting operation can frequently be eliminated.

It is possible to combine the mordanting and oxidizing steps by employment of suitable solutions. The aluminum bronze powder can be boiled with slightly acidified solutions of ferric chloride or acetate, aluminum chloride, acetate or sulfate, stannous chloride or chromic acid, for example; the acidity of these solutions being adjusted to produce the desired oxidizing effect. The surface thus produced is in excellent condition for dyeing.

The aluminum bronze powder can usually be cleaned, mordanted and oxidized in one operation, for example by the introduction of an organic cleaner, such as an alcohol, into the mordanting and oxidizing bath.

After the surface has been properly treated the aluminum bronze powder may be dyed by methods suitable for producing the gold shades of my invention. Mixed dyes may be used. It has been found, for example that the dyes known by the names of brilliant green and auramine or mixtures thereof will produce the desired gold colors. Other gold tints can be obtained by admix-

ing therewith other dyes of varying shades, such as rhodamine, or the like.

Other aniline or lake-forming dyes can be employed.

The dyeing is advantageously accomplished in the presence of water-soluble inert organic solvents in which the dyes are soluble. Methanol, ethyl alcohol, diethylene glycol, a mixture of ethyl and methyl glycols, the ethyl ether of ethylene glycol, dioxan, etc. can be employed. A mixture of ethylene glycol mono ethyl ether and dioxan can be employed with tannic acid in the dye bath if desired.

After the dyeing operation it is important that the colors be fixed by suitable fixing agents in order that they may be light-fast. These fixing agents can be conveniently added directly to the dye bath or a separate operation may be used. Suitable fixing agents are sodium tungstate, tartar emetic, sodium phosphate, zinc acetate, calcium acetate, alkali metal chromates and dichromates, soluble titanium salts, such as the oxalate and sulfate, soluble zirconium salts, and the like.

The chromates and dichromates are valuable fixing agents since they produce a noticeable deepening of the golden shade of the powders. They also produce an important increase in the light-fastness of the colors. It is believed that this may be due to the chromium compounds acting as a light filter, serving to exclude the ultra violet light. The bronze powders may be treated with chromate solutions either before or after dyeing.

My invention may be illustrated by the following specific embodiments which represent actual commercial operations for the production of the gold bronze powders of the present invention.

Example 1.—Apple green gold

To 160 parts of aluminum casting, made into aluminum bronze powder by usual methods, there was added 6 parts tannic acid U. S. P., 5 parts brilliant green cryst. pwd. and 150 parts methanol. These components were mixed. There was then added 12.5 parts fixing solution. After mixing, 1 part of tartar emetic dissolved in 1 part water was added and mixed. Then there was slowly added 150 parts of water which served to precipitate the dye on the powder. The liquid was filtered off from the dyed powder and the latter was dried. The powder (weighing about 160 oz.) was finally polished with 2 tablespoons of lard in the usual manner.

Example 2.—Leaf green gold

160 parts aluminum bronze powder were mixed with 6 parts tannic acid, 3 parts brilliant green cryst. pwd., 2 parts auramine D. O. Conc. and 150 parts methanol. To this mixture there was added 12.5 parts fixing solution. Then 1 part tartar emetic dissolved in 1 part water was added. This mixture was stirred and 150 parts water were slowly added while stirring. The dyed powder was recovered, dried and polished.

Example 3.—Gold light shade

In this example 80 parts of the aluminum bronze powder, 10 parts auramine O, 2 parts rhodamine B Ex., 4 parts tannic acid and 16 parts denatured alcohol were mixed. To this was added a fixing solution and finally 16 parts water with stirring. The dyed powder was recovered and further treated in accordance with the preceding examples.

Example 4.—Gold deep shade

In this example 80 parts of the aluminum bronze powder, 4 parts auramino, O, 0.25 part brilliant green, 4 parts tannic acid and 16 parts denatured alcohol were employed in the dyeing operation. The dyed powder was further treated in accordance with the preceding examples.

The particular fixing agent employed in the preceding examples was made by dissolving 100 parts of sodium tungstate in 150 parts cold water. To this solution 28 parts 66° Bé. sulfuric acid and 32 parts water were slowly added. A gelatinous precipitate was seen to form. The solution was boiled while stirring until the precipitate dissolved and there was then added 15 parts disodium phosphate and 10 parts sodium acetate. The solution was again boiled and sufficient cold water added to make a total of 500 parts.

The bronze powders of the present invention are useful in all the various applications in which bronze powders of the prior art have been employed. These applications include all types of printing and lithographic operations, as well as the production of gold finish on picture frames, farm and garden tools, hardware of all descriptions, labels, wallpaper, etc. On account of the non-flaking characteristics of these powders it is usually possible to dispense with the varnish coating which is usually applied over gold bronze powders. The new powders are not only non-tarnishing, they are also rust-preventing.

While the above description includes what are considered to be the best embodiments of the present invention, there are various modifications which can be made which fall within the scope thereof. For example various other coloring agents or dyes can be employed in the process of the present invention. These include oil soluble colors, sudan colors, zapon, fast colors and acid colors such as acid violet, acid green and neptune blues. Suitable inert organic solvents are readily available for the use of these colors. Other modifications within the scope of the following claims will be immediately evident to those skilled in the art.

In the following claims the statement that the dyed powder is separated from the bath liquid "by a mechanical method" is intended to include those methods, such as filtration, decantation, etc., which are conducted without evaporation of the bath liquid.

What I claim is:

1. In the manufacture of substantially light-fast gold bronze powders, the process which comprises simultaneously mordanting and dyeing an aluminum bronze powder in the presence of a water soluble inert organic solvent, adding an aqueous fixing solution and water and recovering the resulting dyed powder by a mechanical method.

2. The process of claim 1 wherein the said powder is dyed by a dye selected from a class consisting of brilliant green and auramine.

3. The process of claim 1 wherein the said powder is dyed by a dye selected from a class consisting of brilliant green and auramine mixed with rhodamine thereby producing gold colors of varying shades.

4. In the manufacture of substantially light-fast gold bronze powders, the process which comprises mixing together an aluminum powder coated only with a natural oxide film, tannic

acid, alcohol, and an alcohol soluble, aniline dye selected from a class consisting of brilliant green and auramine, then adding a fixing agent and water to precipitate the dye on the powder, separating the resulting dyed powder from the liquid by a mechanical method, drying and polishing.

5. In the manufacture of substantially light-fast gold bronze powders, the process which comprises mixing powdered aluminum, coated only with a natural oxide film, with a solution of a mordant and of a dye in an inert water-soluble organic solvent, said dye being selected from a class consisting of brilliant green and auramine, then precipitating the dye on said powder by the addition of a solution of sodium tungstate and water, and recovering the resulting dyed powder.

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