

Patented May 6, 1947

2,420,262

UNITED STATES PATENT OFFICE

2,420,262

METHOD OF REMOVING FIRE FILM FROM
HEATED SILVER-COPPER ALLOYS

Malio Navaretta, Providence, R. I.

No Drawing. Application December 29, 1945,
Serial No. 638,458

4 Claims. (Cl. 134-3)

1

My invention relates to improvements in the method of brightening silver particularly for removing all traces of "fire film" from objects constructed of pure silver, sterling silver, or other silver alloys particularly those containing copper.

When a silver article is heated particularly one containing copper, as is necessary when soldering parts together, it gets what is called in the trade a "fire" which is a black film probably a mixture of soot, silver nitrate, silver oxide, etc. In the prior art it has been customary to subject such "fire" covered articles to what is called a "pickling" dip which consists of pickling them in a hot dilute sulphuric acid bath in dilutions of the ratio of 10% commercial sulphuric acid to 90% of water. After the pickling dip, the black fire film turns white and the fire covered silver articles are then dipped in commercial nitric acid cold which causes the film to dissolve. It is believed that the "pickling" dip removes the carbon from the film and the nitric acid "fire" dip the silver nitrate and to a large extent the silver oxide leaving, however, on the article a milky "fire film" which may consist of remaining silver oxide or other impurities on the article. Various attempts have been made in the prior art to remove all traces of the "fire film" namely this film which remains after the common prior art treatments of a hot acid pickle and a cold or hot nitric fire dip. It has been the practice to attempt to remove traces of this "fire film" by a so called cyanide dip which comprises a solution of 3 to 15 ounces of sodium cyanide per gallon of water. While this removed to a certain extent all traces of redness from the film it did not remove all traces of whiteness. After the cyanide dip the articles are usually rinsed off or cleaned with the usual ammonia or other rinse.

Prior to my invention to remove all traces of "fire film" it has been customary in the jewelry art to scratch brush or burnish with steel balls or soap all traces of "fire film" from the articles, usually by scratch brushing. This is a slow, laborious and expensive hand process, thus with one jewelry plant employing 20 solderers it has taken three or four men two or three days to scratch brush one day's work. With my invention this is entirely eliminated and the "fire" and "fire film" entirely removed and articles bright-

2

ened by said 20 solderers within the course of an hour, after a short day's work is completed.

In addition to removing the film it is desirable to brighten the silver articles and while the silver articles were brightened to a certain extent by the cyanide dip, it has remained for my invention to not only remove all traces of "fire film" but also to give the article the desired brightness, a feature not successfully accomplished in the prior art.

To these ends, after the usual hot pickling dip and nitric dip, the present inventor has discovered that if a peroxide dip be inserted prior to the usual cyanide dip that all traces of "fire film" will be removed and the articles successfully brightened in a commercial manner.

A further object of my invention therefore, is to brighten silver articles whether or not they have "fire film" on them.

Having now described my improved process broadly, I will now describe in detail how my invention may be carried out.

When my invention is used to remove "fire," the immersion hot pickling dip which is well-known in the art comprises immersing the articles in hot dilute sulphuric acid solution preferably diluted to about a 10% solution of commercial sulphuric acid is employed. As explained above, the "fire" remaining on the silver articles after the heat treatment usually comprises a black film and the pickling dip has tended to remove the carbon or blackness from the film leaving a white film thereon.

I then according to prior art practice, treat the articles with a cold nitric acid "fire" dip which may, however, if desired, be applied hot, of commercial nitric acid varying from 36° to 42°, which as stated, to a large extent oxidizes off the silver nitrate and other impurities.

However, after such prior art treatments there has often remained a milky film called in the trade a "film of fire" and it is to the removal of this film that my invention particularly relates. I have attained entirely satisfactory commercial results by using a solution of 90 to 120 cc. or 3 to 4 ounces of hydrogen peroxide of a 10% concentration, the amount of which, however, may be varied depending on the concentration of the solution and one-half ounce sodium cyanide which may be increased up to 2 ounces dissolved

3

in 10 to 50 times their volume of water, in the preferred embodiment to a gallon of water until the articles turn pink which indicates the removal of all traces of the silver oxide and other white impurities. The requisite amount of water is first set aside and the sodium cyanide which comes in ounce balls commercially is broken up and dissolved in it. The peroxide in the desired amount is preferably not poured in the cyanide solution until just prior to the immersion of the articles therein so as not to break up the peroxide to any great extent prior to the introduction of the articles. The articles are then immersed in the solution and a violent ebullition and discharge of oxygen takes place as the H_2O_2 decomposes into water and oxygen which oxidizes off all the impurities in the film except the pinkish copper residue particles. While this solution will have a greater reaction if used fresh each time, I have found in practice that it may be used three or four times before it is necessary to replenish it. The applicant has tried out all different proportions in the ranges set forth above and knows they will all work commercially with varying degrees of violent reaction depending on concentration.

Examples

1. 90 cc. or 3 ounces of 10% H_2O_2 , one-half ounce sodium cyanide per gallon of water.
2. 90 cc. or 3 ounces of 10% H_2O_2 , one-half ounce of sodium cyanide per one-half gallon of water.
3. 120 cc. or 4 ounces of 10% H_2O_2 , one-half ounce sodium cyanide per gallon of water.
4. 120 cc. or 4 ounces of 10% H_2O_2 , one-half ounce sodium cyanide per one and one-half gallons of water.
5. 60 cc. or 2 ounces of 10% H_2O_2 , one-half ounce sodium cyanide per gallon of water.
6. 150 cc. or 5 ounces of 10% H_2O_2 and 2 ounces of sodium cyanide per gallon of water.

It will be seen therefore that the proportions by volume of 10% H_2O_2 vary to the sodium cyanide respectively from 8 to 1 to 3 to 2 and the proportion of the two together to the requisite amount of water vary from 10 to 50 times the volume of water to volume of chemicals. After this immersion in any of the solutions heretofore described, the articles turn pink, indicating that all traces of silver and other white or black impurities are removed, leaving in the film red-dish copper or other impurities.

I then immerse said articles at least once in a standard cyanide dip which comprises 3 to 15 ounces of sodium cyanide balls or powder per gallon of water preferably 6 ounces and immerse the articles in said bath until all red traces disappear thus removing all traces of copper from the "fire" residue. Both the peroxide dip and the cyanide dip brighten the articles. Sterling silver is an alloy of copper and it is necessary to remove the silver impurities as well as the copper impurities, the silver impurities being removed by the peroxide dip and the copper impurities being removed by the cyanide dip. My improved method or solution however, may be used to brighten pure silver or other silver alloy than sterling silver.

I employ the word silver in the claims to include pure silver, sterling silver alloy containing silver and copper or other silver alloys.

If the film is not completely removed, the immersions in the peroxide and cyanide baths are successively repeated and for this purpose it is

4

not necessary to renew the peroxide bath until the articles are sufficiently brightened when they may be subjected to a final rinse in the peroxide solution. In most instances, however, all traces of "fire film" are removed and the articles sufficiently brightened by one peroxide and one cyanide dip.

The articles may be washed in any manner known in the art such as with a well-known ammonia rinse comprising 2 ounces dry soap powder, 4 ounces 26 degree Baumé ammonia in 4 gallons of water, although the proportions and nature of the final rinse may be varied in any manner known in the art.

As stated hitherto, my improved peroxide solution may be employed to brighten silver as well as to remove "fire" therefrom in association with the usual cyanide dip, it being a characteristic feature of my invention that these two dips are used together particularly with sterling silver.

It is apparent that I have provided a novel method for brightening silver and/or removing all traces of "fire" and "fire film" from silver articles and solutions for use therewith with the advantages explained above.

It is understood that my invention is not limited to the methods or solutions described and that various deviations thereof may be made without departing from the spirit and scope of the appended claims.

What I claim is:

1. The method of removing "fire" from heated silver-copper alloy articles comprising pickling said articles with a hot dip of dilute sulphuric acid to remove the carbon, treating the articles with a nitric acid fire dip to oxidize off the silver nitrate, leaving a milky "film of fire," immersing said articles at least once in an aqueous solution containing when prepared hydrogen peroxide equivalent to 90-120 cc. of 10 per cent of hydrogen peroxide solution and substantially one-half ounce sodium cyanide per gallon of water until said articles turn pink to remove all traces of silver oxide, immersing said articles at least once in a solution of 3-15 ounces of sodium cyanide per gallon of water until the red disappears thus removing all traces of copper from the sterling silver alloy residue, and washing the articles with an ammonia rinse, comprising ammonia, soap and water.

2. The method of removing "fire" from heated silver-copper alloy articles comprising pickling said articles with a hot dilute sulphuric acid dip to remove the carbon, treating the articles with a nitric acid fire dip to oxidize off the silver nitrate, leaving a milky "film of fire," immersing said articles at least once in an aqueous solution containing when prepared hydrogen peroxide equivalent to from 60 to 180 cc. of 10 per cent hydrogen peroxide solution and sodium cyanide in amounts varying from $\frac{1}{3}$ to 2 ounces per gallon of water until said articles turn pink to remove all traces of silver oxide, immersing said articles at least once in a solution of 3-15 ounces of sodium cyanide per gallon of water until all red or pinkish tint disappears thus removing all traces of copper from the sterling silver alloy residue, and washing said articles with an ammonia rinse, namely with ammonia, soap and hot water.

3. The steps in the method of removing "fire" from heated silver-copper alloy articles or otherwise brightening silver articles comprising immersing said articles at least once in an aqueous solution containing when prepared hydrogen

2,420,262

5

peroxide equivalent to 90-120 cc. of 10 per cent of hydrogen peroxide solution and one-half ounce sodium cyanide per gallon of water until said articles turn pink to remove all traces of silver oxide, and immersing said articles at least once in a solution of 6 ounces of sodium cyanide per gallon of water until the red disappears thus removing all traces of copper from the residue.

4. The method of removing "fire" from heated silver-copper alloy articles or otherwise brightening silver articles comprising immersing said articles at least once in an aqueous solution containing when prepared hydrogen peroxide equivalent to from 60 to 180 cc. of 10 per cent hydrogen peroxide solution and sodium cyanide in amounts varying from $\frac{1}{3}$ to 2 ounces per gallon

6

of water until said articles turn pink to remove all traces of silver oxide, and immersing said articles at least once in a solution of 3-15 ounces of sodium cyanide per gallon of water until all red or pinkish tint disappears thus removing all traces of copper from the residue.

MALIO NAVARETTA.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

15	Number	Name	Date
	838,810	Roome	Dec. 18, 1906