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METHOD OF BRIGHTENING METALS ELECTRONEGATIVE TO IRON

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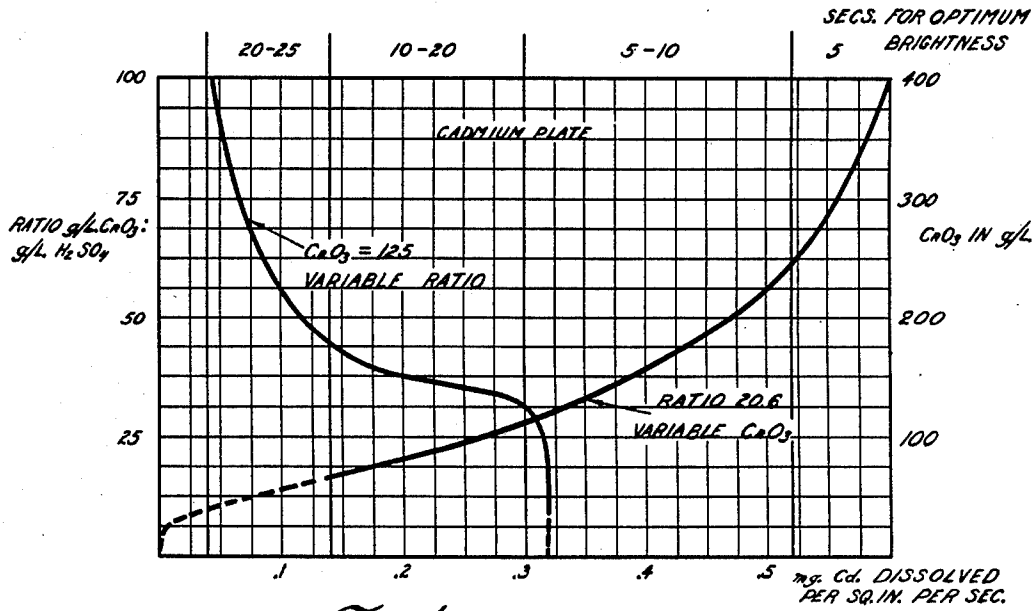

Fig. 1

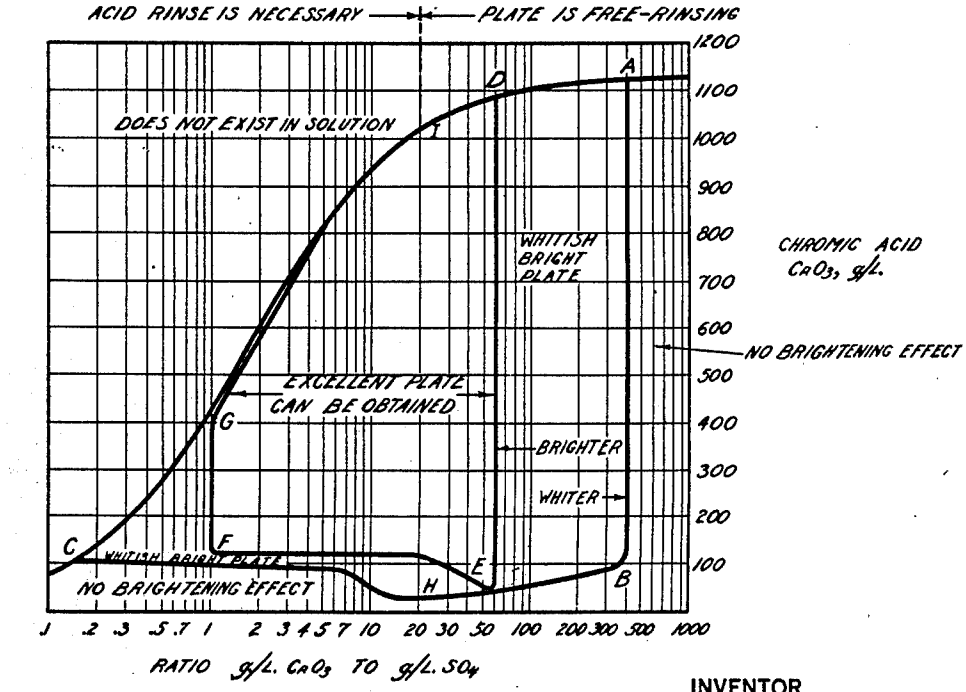

Fig. 2

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METHOD OF BRIGHTENING METALS ELECTRONEGATIVE TO IRON

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7 Claims. ~~(Cl. 148—6)~~ 148 – 6.21

This invention relates to a method of treating metals electronegative to iron and belonging to the second sub-group of the second group of the periodic system as given on pages 522–3 in the 16th edition of "Handbook of Chemistry and Physics" by Hodgman and Lange, to improve the surface appearance and produce a high lustre, and in particular to a method of treating a coating of a metal electronegative to iron such as cadmium and zinc to give the coating a high lustre.

In the plating of these metals which are electronegative to iron, in particular such as cadmium and zinc, it is common practice to use addition agents in the plating solution which tend to produce deposits which are bright and lustrous. The lustre which is sometimes imparted to cadmium plate is very similar to that obtained by buffing. In the case of articles which have an irregular surface contour the metal coating in the recesses does not have the same high lustre as that on the protruding parts. Very often the electrodeposited coatings in these recesses are dull owing to too high or too low a concentration of the addition agent or that the addition agent is insufficiently active. Hence, it has been proposed to dip the article subsequent to the plating operation in a brightening dip. Among the various dips which have heretofore been proposed are solutions of non-oxidizing acids such as acetic, oxalic, cyanic and weak solutions of sulphuric and hydrochloric acids, but a solution of any one of these acids only has a whitening effect on metals electronegative to iron such as cadmium and zinc. This whitening effect is probably due to removal of a thin film of oxide from the surface and is distinct from, and should not be confused with, the brightening or obtaining of a high lustre on the surface of cadmium or zinc coatings. It has also been proposed to use dilute nitric acid as a dip for producing a bright or a highly lustrous cadmium coating, but this dilute nitric acid solution has the disadvantage of accelerating or causing tarnishing of the cadmium surface.

It is an object of this invention to produce a method and dip for brightening metals which are electronegative to iron and in particular such metals as cadmium, zinc and magnesium without causing the metals to tarnish.

It is an object of this invention to produce a method and dip for brightening electrodeposited coatings of metals electronegative to iron which have been electroplated from a cyanide bath, such as cadmium and zinc.

This invention also contemplates a method of treating metals electronegative to iron by immersion in a dip containing chromic acid CrO_3 and an active acid radical of the nature of a catalyst and also the production of this type of brightening dip.

We have discovered that an aqueous solution of chromic acid, to which has been added a proportion of certain active acid radicals, gives a very satisfactory lustre to dull surfaces of cadmium and zinc which may be electrodeposited, sprayed, rolled, cast, etc., as well as to rolled magnesium strips. These active acid radicals include the sulphate, the chloride and the nitrate radicals.

Pure chromic acid solutions do not brighten the plate. This fact is undoubtedly related to their inability to dissolve cadmium, zinc and magnesium. The addition of active acid radicals causes an attack on the metal. These active acid radicals act in the nature of catalysts. Inactive radicals do not generally cause solution of the plates. The pure chromic acid with or without the addition of inactive radicals may have a slight whitening effect similar to that of a number of weak acid solutions, but this effect should not be confused with the brightening effect which is obtained by means of our invention. It appears as if certain crystal faces in the surface are attacked preferentially to others in our solution, thereby greatly increasing the reflectivity of the surface and producing a brilliancy similar to that of a buffed surface.

The accompanying graph, Figure 1, which is practically self-explanatory shows that the rate of solution of the cadmium plate increases with increasing chromic acid and acid radical contents. This figure also shows that the desired time in seconds of immersion in the brightening solution of the metal which is to be brightened, decreases with the increasing rate of solution of the plate. In other words, excellent brightness is associated with a relatively high rate of solution.

Referring to the graph shown in Figure 2, it will be seen that the ratio of the chromic acid to the acid radical content is important. When this ratio in grams per liter of chromic acid (CrO_3) to grams per liter of sulphate radical (SO_4) falls below about 20 (i. e. when the grams per liter of chromic acid is less than twenty times the grams per liter of sulphate radical) a brown film consisting probably of chromium chromate which is insoluble in water is formed on the surface of the cadmium coating. This film can be

removed by rinsing the surface of the cadmium coating in any weakly acid solution such as dilute sulphuric, hydrochloric or acetic acid. When the ratio of chromic acid in grams per liter to sulphate radicals in grams per liter is above about 20, no insoluble film is formed and the brightened cadmium metal can be rinsed in water and the acid rinse is unnecessary. This critical ratio at which the brown film forms on the cadmium is not absolutely 20 but ranges above and below 20 a few points and in general between about 18 and 22.

Figure 2 shows the relation between the appearance of the plate and the composition of the solution. This chart is based on experiments at ordinary room temperature. The effect of increasing the temperature is not particularly great except that it moves the area within which bright plates are obtained to include higher ratios.

In general, a distinct brightening effect can be obtained with from 25 grams per liter chromic acid up to the saturation point when the ratio falls below 1 and 400. At the extremities of the ratio range, higher chromic acid content is desirable, such as 100 grams per liter at a ratio of both 1 and 400.

The most effective ratio falls between 1 and 60, with a desirable chromic acid content from 125 grams per liter and up at a ratio of 1 and 50 grams per liter and up at a ratio of 60.

As the rate of solubility of the cadmium plate increases with the chromic acid content and the thickness of the plate is originally rather low (in the order of .0002–.0010 in.), we prefer to use a moderate chromic acid content. This is all the more advisable from an economic standpoint since the solution clings to the plate and considerable quantities may be lost as "drag-out" in the subsequent rinsing operation. Our preferred solution for work plated in still tanks and automatics, therefore, consists of 150 grams per liter chromic acid (CrO_3) plus 3.75 grams per liter sulphuric acid (H_2SO_4) which is equal to a ratio of about 40. A 5 to 10 seconds immersion in this solution is sufficient to bring forth the desired lustre. No acid rinse is necessary following the immersion in this bright dip.

Work plated in bulk in barrels cannot be handled as fast as other work and therefore the time of attack on the coating is longer. We, therefore, prefer to use a weaker dip for barrel plated work, containing 100 grams per liter chromic acid (CrO_3) and 2 grams per liter sulphate radical (SO_4), giving a ratio of 50.

Chloride (Cl) or nitrate (NO_3) radicals can be substituted for the sulphate radical without materially changing the conditions. These radicals are perhaps slightly less active and the ranges of concentrations not quite as wide. The critical ratio of chromic acid to active acid radical, below which acid rinses must be employed to remove the brown film from a cadmium coating, falls at about 10 for Cl and at about 12 for NO_3, when grams per liter is chosen for the unit.

The general description of the action of our new dips on cadmium plate is also applicable to their action on zinc plate. The lustre obtainable on zinc plate is not quite as brilliant as that on cadmium plate. This is probably a consequence of the difference in physical properties of the metals themselves. It is well known that buffed cadmium plate has a higher lustre than buffed zinc plate.

The ratio of chromic acid to sulphate radical concentrations, above which the dip is free rinsing and no acid rinse is needed, is practically the same for zinc as for cadmium plate. When the chloride radical is used, this limiting ratio has such a high value, above that of the best ratios for obtaining a high lustre on the zinc coating that a rinse in dilute acid appears necessary to remove the brown film.

We have found that a mixture of active acid radicals can be used just as well as single active acid radicals. The effect of the various radicals appears to be additive.

The reaction with the metals that are brightened causes a reduction of the chromic acid to trivalent chromium. As the solution is used, the trivalent chromium content increases, and finally reaches a concentration which causes a brown coating, which is insoluble in water, to form on the metal. In our preferred solution containing 150 grams per liter chromic acid (CrO_3) and 3.75 grams per liter sulphate radical (SO_4), the maximum allowable concentration of trivalent chromium is about 10 grams per liter, corresponding to the solution of about 40 grams per liter of cadmium. For continuous operation, it is therefore desirable to re-oxidize the trivalent chromium to hexavalent. This is successfully done by means of the porous cup method used for a similar purpose in chromium plating solutions.

The chromic acid bright dip can also be used for brightening of plate which has been in use for a period of time and has become tarnished, stained and dirtied. The dilute nitric acid bright dip which has been proposed heretofore, on such a plate causes dirty dark spots on the immersion of even partially dry or dirty surfaces.

This dip of chromic acid and an active acid radical, as above described, not only brightens metals electro-negative to iron and belonging to the second sub-group of the second group of the periodic system, but also prevents tarnishing of these metals when plated from a cyanide solution as described and claimed in copending application Serial No. 627,423.

Although the method has been particularly described in reference to brightening the surfaces of electrodeposited metals electronegative to iron and belonging to the second sub-group of the second group of the periodic system, it is specifically understood that the above set forth method and dip for brightening the surfaces of these metals is applicable to the surfaces of these metals whatever their genesis may be, that is, whether electrodeposited, sprayed, rolled, cast or otherwise formed.

We claim:

1. A method of treating cadmium to produce a high lustre comprising immersing the cadmium in a solution of chromic acid and a sulphate radical and maintaining the ratio in grams per liter of chromic acid to sulphate radical above a critical ratio of about 20.

2. A method of treating cadmium to produce a high lustre comprising immersing the metal in a solution containing 150 grams per liter chromic acid and 3.75 grams per liter of sulphuric acid.

3. A method of treating cadmium to produce a high lustre comprising immersing the metal in a solution containing 150 grams per liter chromic acid and 3.75 grams per liter of sulphuric acid for a period of about 5 to 10 seconds duration.

4. A method of treating cadmium to produce a high lustre comprising immersing the metal in a solution containing 100 grams per liter chromic acid and 2 grams per liter of sulphuric acid.

5. A method of treating metals electronegative to iron and belonging to the second sub-group of the second group of the periodic system to produce a high lustre comprising immersing the metal in a solution of chromic acid and a catalyst in the form of a sulphate radical and maintaining the ratio in grams per liter of chromic acid to sulphate radical above a critical ratio of about 20, or maintaining an equivalent ratio in grams per liter of chromic acid to an acid radical or radicals equivalent to the sulphate radical above an equivalent critical ratio.

6. A method of treating cadmium to produce a high lustre comprising immersing the cadmium in a solution of chromic acid ranging in concentration from 25 grams per liter of solution to the saturation point and a catalyst in the form of a sulphate radical and maintaining the ratio in grams per liter of chromic acid to sulphate radical within a range from above a critical ratio of about 20 to a ratio of 400 or maintaining an equivalent ratio in grams per liter of chromic acid to an acid radical or radicals equivalent to the sulphate radical within a range from above an equivalent critical ratio to a ratio of 400.

7. The method as set forth in claim 5 with the additional step of maintaining the concentration of the trivalent chromium below the point at which a brown coating insoluble in water is formed on the metal whereby continuous operation of the bath is permitted.

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