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Composition and Comparison of Zinc Electroplating Solutions

COMPOSITION AND COMPARISON OF ZINC ELECTROPLATING SOLUTIONS

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INTRODUCTION

There is apparently a real need for a good, effective, but cheap, zinc electro-plating solution for commercial work, for despite the number of formulas to be found in the journals and the number of commercial solutions on the market, there is only one which the large users of zinc-plating solutions agree is satisfactory in every respect. This is the solution which was put on the market in 1905 by the Meaker Co., of Chicago. The makers have not patented the formula, but have managed to keep its composition a secret, in spite of the many attempts, which have been made at various times by different users, to analyze it.

Some of the advantages claimed for this solution are that it gives a good, fine-grained, well-adhering coating of zinc on iron and steel; it is neutral, efficient, and self-sustaining,-all that is necessary to keep it in continuous operation being the occasional addition of sulfuric acid, and during the course of a year, the addition of ten per cent of fresh solution to the bath. (The necessity for the latter seems to be a question with the users.) Moreover, it is claimed that it can be operated successfully using as high a current density as 60 amperes per square foot of cathode surface, which is much higher than can be used with other solutions. This is a great advantage, as it means that the same thickness of deposit can be obtained in fifteen minutes with this solution as that obtained in an hour and forty-five minutes with a solution where the current density is limited to ten amperes per square foot.

The only objection to the Meaker solution is the price.

It sells for more than other solutions, but since no other plating bath will give good results, there is no difficulty in selling it.

Undoubtedly a large part of the material in the solution has been added, not because it is necessary to insure good operation, but merely to prevent analysis. Accordingly, it was decided to analyze the solution, so far as possible, and using the same electrolyte as that found by analysis to be the basis of the Meaker solution, try the effect of several addition agents

The chief use for zinc-plating is in the deposition of a thin layer of the metal on iron and steel to protect them from corrosion. Zinc has the advantage over tin for this purpose in that it is electro-positive to iron (+.493 to -.16)[1] so that in case a part of the iron becomes exposed and wet, zinc tends to dissolve in place of the iron.

The coating of zinc may be applied to the metal either electrolytically or by one of the many so called hot processes, such as dipping, sherardizing, spraying, etc. The dipping method, or some modification of it, is probably the most generally used, but, while the zinc thus deposited is generally brighter and more pleasing in appearance than that deposited electrolytically, it has been shown that the latter protects the iron much more thoroughly.

The excessive amount of zinc required by the hot galvanizing industry in the early days led to the adoption of means for smoothing or wiping the deposit in order not only to save the

zinc, but also to secure a smoother and more uniform coating. This, however, is only possible with sheets, wire, and a few products which can be passed continuously through the bath. The wiping is held by some authorities to constitute a serious objection to the hot-galvanizing process, in that it is said to decrease the lasting qualities of the coating, while if the wiping is not employed, the expense of the galvanizing is enormously increased and some grades of product cannot be subsequently manufactured in suitable finished form. Moreover, the losses due to the formation of dross and skimmings also increase the cost of the process.

Although the Sherardizing process[2], which consists in heating the articles to be coated in zinc dust, has been widely exploited in this country since its introduction in 1904, it has not come into extensive commercial service. The coating formed by this process is rich in iron and not altogether pleasing in appearance. Moreover, the process does not lend itself well to continuous operation, i. e., goods cannot be cleaned and galvanized in continuous process.

Articles which require bending after galvanizing cannot be given continuous coatings by hot processes with any certainty that such coatings will adhere and withstand bending operations without cracking. Moreover, with hot processes, the thickness of the deposit cannot be regulated to any extent, while with the electrolytic method, the thickness of the deposit can be regulated very exactly.

Although the galvanizing process probably had its origin about 1820,[3] it is not until 1829 that we find any mention of

electro-galvanizing. [4]In that year Dr. Jno. Revere, of New York brought before the Lyceum of Natural History, of that city, samples of zinc coated spikes and small plates attached to wood, the whole having been exposed to the action of sea water since 1827. Revere was convinced that the coating of zinc formed an excellent protection for iron articles. The mention of electrochemical terms in Revere's work indicates that the coating was accomplished by electro-galvanizing methods. However, the first patents relating to this process were not issued until 1852, when[5] Wall patented a solution for "electrically depositing zinc upon iron by means of Voltaic batteries." [6]Other early patents show that the problem of electro-galvanizing received considerable study.

However, the extensive use of electro-galvanizing in the early days was not practicable owing to the limited current available from batteries. Electro-plating requires the use of an electric generator supplying current of high amperage at low voltage, and it has required many years to develop this type of generator and give it a fair degree of efficiency. The possibilities of electro-galvanizing have therefore been unappreciated until recent times.

After the invention of the generator there was a revival of interest in electro-galvanizing, as is shown by the number of patents[7] issued and the number of formulas for zinc plating solutions that appeared in the journals. Between 1880 and 1903 there were forty-nine patents, mainly for solutions, issued in England, France, Germany and the United States. In these solutions, the zinc salts most generally used for the electrolyte

are the sulfate and the chloride, the greatest range of difference being in the addition agents suggested.

Of these agents for improving the quality of the deposit and lasting qualities of the solution, colloids[8] and glucosides[9] seem to be mose generally accepted as satisfactory, although in going through the journals for the last fiftenn years one finds no less than forty different substances, varying in composition from the simple salts of sodium, aluminium, etc., to the most complex organic compounds.

Watts and Shape[10] seem to have been the only ones to make a systematic study of various addition agents. They tried out forty-two different substances, using a bath containing twenty-five percent zinc sulfate and one gram per liter of an organic compound. An iron cathode and zinc anode were used, the bath being kept at 22° C., and current passed for two hours at a current density of 1.1 amperes per square decimeter of cathode surface. Of the substances tested, beta-napthol and pyrogallol gave results which compared most favorably with those obtained from Meaker solution under the same conditions.

EXPERIMENTAL.

I. Analysis.

Qualitative.

The Meaker zinc-plating solution is a clear colorless solution. On standing, brown, spongy particles similar to the material deposited by iron water, separate out. The solution is very faintly acid to litmus.

1. A qualitative analysis[11] was made of the solid material obtained by evaporation of the Meaker solution, for the metals and acids.

2. A liter of the Meaker solution was distilled, the distillation being continued until the residue remaining in the flask began to char. The greater part of the distillate came over at 100°C., and was plain water. Between 100° and 105° C. about 5 cc. of distillate was collected which was acid to litmus and showed traces of sulfate. Material remaining in flask smelled of glue when charring began.

3. An ether extraction was made of the solid residue remaining in the flask after distillation. This extraction gave less than .3 gm. of solid matter which was apparently a complex mixture of organic substances, and could not be separated. The material was dark brown to black in color, of a gummy nature, and had a smell resembling somewhat, that of licorice.

4. A half-liter of the Meaker solution was distilled by steam distillation. The distillate was neutral to litmus and smelled strongly of glue, when hot. On cooling, a fair amount of a light brown colloidal substance settled out. This material gave all indications of glue.

The results of the qualitative analysis are shown in table I, below:

TABLE I

Results of Qualitative Analysis.

Substance.	Amount.
Zinc	large quantity.
Iron	small quantity.
Sulfates	large quantity.
Glue	small quantity.
Organic matter (nature could not be determined)	fair quantity.

These results indicate that the electrolyte is a rather concentrated solution of zinc sulfate, containing some iron, perhaps as an impurity, and a rather large amount of organic matter including a small quantity of glue. Part of this organic matter has undoubtedly been added to the solution as "addition agent" for improving the quality of the deposit. The glue is probably for this purpose. However, the large quantity of organic matter present would seem to indicate that the greater part has been added merely to interfere with the analysis of the solution.

I. Analysis.

Quantitative.

1. Solid material in solution.

The quantity of solid material in solution was determined by evaporating 500 cc. of the Meaker solution in a porcelain dish on the steam bath.

During the evaporation a sweetich, vinegar-like smell was noticed which was thought to be due to acetic acid, but subsequent analysis failed to show the presence of this acid.

As the evaporation proceeded the solution became more strongly acid.

The residue, after evaporation, was partly composed of neelde-like, colorless crystals (probably zinc sulfate), and the remainder was a white, non-crystaline solid.

2. Loss on ignition.

Some of the residue from the evaporation of the solution was finely ground in a mortar, dried in an oven of 100°C. and cooled in a dessicator. This material was used in all the analyses. Duplicate samples of this material were ignited in porcelain crucibles over the Bunsen flame, then over the blast lamp to constant weight.

3. Determination of iron.[12]

Duplicate samples of the ignited residue from the "loss on ignition" determination, were weighed out and dissolved in aqua regia. The solution was evaporated to dryness on the water bath, taken up in about two cubic centimeters of concentrated hydrochloric acid, diluted, and filtered from a trace of insoluble matter. Two gm. of NH_4CL was added to keep the zinc in

solution, then the iron was precipitated from this solution as ferric hydroxide, in the usual manner, dissolved in hydrochloric acid and reprecipitated, to insure absence of zinc in the precipitate.

The precipitate was then filtered, dried, ignited over the Bunsen flame and weighed as ferric oxide.

4. Determination of Zinc.[13]

The zinc was determined on the filtrate from the iron determination by the method recommended by H. Tamm[14] and improved by Lösekann[15] and Meyer, Austin[16], and Dakin[17].

The filtrate from the iron precipitation was evaporated to a volume of 100 cc., neutralized with hydrochloric acid and the zinc precipitated from the hot solution with diammonium phosphate as zinc ammonium phosphate, filtered, dried, and weighed.

5. Determination of Sulfates.[18]

The sulfates were determined by precipitation as barium sulfate from the solution of the solid residue from evaporation.

The iron was removed before precipitaion of the sulfates, for if this is not done, all of the sulfates are not precipitated from the solution, and considerable iron is thrown down with the barium sulfate. Furthermore the precipitate then loses sulphur trioxide on ignition. The zinc was not removed, as it is occluded to a much less extent than the iron.

The solution of the solid residue in water, was acidified with 5 cc. of dilute hydrochloric acid, and two grams ammonium chloride added to keep the zinc in solution. The iron was then oxidized with nitric acid and precipitated at a temperature of 70°C. as ferric hydroxide, using a liberal excess of ammonia.[19] Under these

conditions the iron precipitate is not likely to contain any basic ferric sulfate, while if the solution is barely neutralized with ammonia, the precipitate will invariably contain some sulfate.

The filtrate from the iron precipitate was exactly neutralized with HCL, then 1 cc. HCL (conc.) was added in excess and the solution diluted to 350 cc. Eight cc. normal barium chloride solution was diluted to 80 cc., the solution heated to boiling and added all at one time to the hot sulfate solution, which was being stirred continuously. (Note: In the presence of ammonium salts the precipitation of the barium sulfate should not be effected, as is otherwise desirable, by the cautious addition of the barium chloride, for this leads to low results, whereas the occlusion caused by the rapid addition of the barium chloride counterbalances this error.)

After the solution had stood for half an hour on a warm hotplate it was filtered, washed with hot water, dried in an oven at 100° C. and ignited in a porcelain crucible over a Bunsen flame. The precipitate of barium sulfate was then weighed. The calculated amount was apportioned to the iron and zinc - assuming that they were present in the original sample as zinc sulfate and ferric sulfate -- and the remainder calculated to sulfuric acid.

6. Organic matter.

Since the qualitative analysis showed the presence only of iron, zinc, sulfate, and a complex mixture of organic matter, the mature of which could not be determined, the total percentage of

organic matter was taken to be the difference between 100 % and the sum of the percentages of iron, zinc and sulfate, in the solid from evaporation.

The results of the quantitative analysis of the solid material from evaporation are given in Table II, below:

TABLE II.

Results of Quantitative Analysis of Solid from Evaporation.

Substance.	Per cent of solid from evaporation.
Zinc	32.94
Iron	.95
Sulfates (as SO_4)	54.61
Organic matter (By difference)	11.50
Total - - -	100.00

Total solid matter (By evaporation) - - 193.7 gms. per liter.

The high percentage of sulfate present in the solid from evaporation indicates that the metals are present in the form of sulfates. Assuming this to be the case, the amount of SO_4 (per cent of total solid from evaporation) required to satisfy the given percentages of zinc and iron was calculated. These two quantities were added together and subtracted from the total amount of sulfates (SO_4) present in the solid, and the difference thus obtained assumed to be the amount of SO_4 present as free sulfuric acid. The results of the calculations, showing the distribution of the SO_4 are given in Table III, on the next page.

TABLE III

Distribution of Sulfate.

Substance	% of total solid	Assumed to be present as -	% of total solid	SO_4 required; % of total solid
Zinc	32.94	Zinc sulfate	81.37	48.41
Iron	.95	Ferric sulfate	3.40	2.40
		Sulfuric acid (By difference)	#3.79	3.79
Total SO_4				54.61

#Calculated from result in last column.

Combining the data from Tables II and III, we may compile a table showing the percentage composition of the solid material in the solution, and with these results, knowing the weight of solid per liter, we may calculate the number of grams of each substance per liter of Meaker solution. Such a table is shown below in Table IV.

TABLE IV.

Composition of Meaker Solution.

Substance	% of solid material-	grams per liter of Meaker Solution-
Zinc sulfate	81.37	158.53
Ferric sulfate	3.40	6.58
Sulfuric acid	3.79	7.34
Organic matter (By difference)	11.44	22.27
Totals -	- 100.00	193.72

The results of the loss on ignition determination on the solid obtained by evaporation of the Meaker solution are of small value in estimating the quantity of organic matter present

with any exactness. Assuming that the residue from the ignition is composed entirely of zinc oxide and ferric oxide, and basing our calculations on the amount of iron and zinc present, we can calculate what the percent of residue should be. The results of such a calculation are shown below in Table V.

TABLE V.

Calculated percentage of " residue from ingition " of " solid from evaporation ", compared with experimental results.

Zinc content, calculated to ZnO	41.01 %
Iron content, calculated to Fe_2O_3	1.36 %
Calculated percent of residue	42.37 %
Percent determined by experiment	45.19 %
Dufference - - - -	2.82 %

This difference is too large to be accounted for by non-volatile impurities such as silica, etc. So it would seem that one or both of the sulfates is not entirely decomposed to the oxide. If this is the case, then the percentage of the loss on ignition for which the sulfates are responsible, cannot be calculated and subtracted from the total loss, in order to find the part of the loss due to the burning out of organic matter. Consequently the results of this determination are valueless, and organic matter must be determined by the difference between the sum of the percentages of zinc, iron and sulfates, and 100 %.

It was thought that the iron comtent of the solution was due to impurities in the materials going to make up the solution. It is very unlikely that chemically pure components would be used.

Such a high content of organic matter in the solution does

not seem necessary, if it is there simply as addition agents, for none of the formulas found in the literature advises the addition of more than a gram or two per liter of addition agent. It seems unlikely that it is present in the form of a zinc salt as a necessary component of the electrolyte, so the only explanation left for its presence is that it is added to prevent an analysis of the solution being accomplished.

II. Plating Tests.

In order to test the effectiveness of several addition agents, some of which, it was suspected, were present in the Meaker solution, a number of electrolytic cells were set up, using as an electrolyte, a solution containing the same quantities of zinc sulfate, ferric sulfate, and sulfuric acid as were found in the solution analyzed.

An attempt was made to duplicate as far as possible, on an experimental scale, the process used by a certain manufacturer who is using the solution in electro-galvanizing iron wire cloth. The specifications obtained from this manufacturer are listed in Table VI, below.

TABLE VI.

Operating Conditions in Commercial Plant
Using Meaker Solution for Plating Iron Wire Cloth.

Electrolyte	Meaker solution
Anode material	Pure zinc
Cathode material	Iron wire cloth
Current density, per sq. ft. of cathode surface	1.[illegible] amperes
Distance between electrodes	6.0 inches
Specific gravity of bath	20° Bé
Temperature of bath	60° to 70° F.

The specific gravity is kept at 20° Bé by the occasional addition of sulfuric acid.

About 10 % of fresh solution is added to the bath during the course of a year.

The cells used for the experimental baths were ordinary glass battery jars, 4 inches wide, 6 1/2 inches long, and 7 inches high. The anodes were sheets of pure zinc, 3 1/2 by 6 in-

ches, immersed to a depth of 4 inches in the solution, and the cathodes, strips of iron wire cloth (obtained from the manufacturer mentioned above) of the same size as the anode. These were also immersed to a depth of 4 inches in the electrolyte, giving an area of one tenth of a square foot of surface in the solution.

In operation the cells were connected in series with a cell containing Meaker solution, the performance of which was used as a basis of comparison for the cells tested. This connection assured similar conditions of current density, temperature, etc., in the cells, so that the comparison of results would be fair.

The cathodes were prepared for plating by first removing all grease from the surface by dipping in a hot 10 % NaOH solution, washing in H_2O, and then removing all scale, oxide, etc., in a "pickle", made up by the following formula:

TABLE VII.[20]

Pickle for Iron.

Substance	Amount
Water	1.0 qt.
Sulfuric acid (conc)	2.8 oz.
Nitric acid	1.2 oz.
Zinc	.2 oz.

This pickle worked very satisfactorily, a few minutes immersion of the iron in the solution being sufficient to thoroughly clean the metal, leaving a good bright surface for plating. After the pickling, the cathodes were placed immediately in the plating bath, to prevent reoxidation.

Current was passed through the cells, first, for a period of one hour, then the cathodes were removed from the plating bath, washed well in water, then polished slightly with a flannel rag and the deposit on the cathode from the test cell compared carefully with the one from the Meaker cell, as to the character of the deposit. The coating was then rated as "good", "fair", "poor", etc., according to how it compared with the check in smoothness, fineness of grain, uniformity, etc.

The cathodes were then cleaned in alkali, dipped in a dilute hydrochloric acid solution to remove any oxide that might have formed, washed thoroughly and returned to the plating baths, and the current passed through the cell for four hours more. At the end of that time they were again removed and examined as before.

The compositions of the electrolytes tested, the conditions under which the tests were run, and the results, are recorded in Table VIII, on next page.

TABLE VIII

Results of Plating Tests.

Electrolyte			Current Density	Time of flow of current	Character of deposit
No.	Substance	Gm. liter of solution -	Amps. ft^2	Hrs.	
1.	Zinc sulfate	158.53	1.0	1.0	Good
	Ferric sulfate	6.58			
	Sulfuric acid	7.34			
	Glucose	5.00	1.0	5.0	"
	Glue	5.06			
	Ammonium acetate	5.00			
2.	Zinc sulfate	158.53	1.0	1.0	Poor, spongy
	Ferric sulfate	6.58	(discarded after first run)		
	Sulfuric acid	7.34			
	Tartaric acid	5.00			
	Dextrine	5.00			
	Glue	5.00			
3.	Zinc sulfate	158.53	1.0		Fair
	Ferric sulfate	6.58			
	Sulfuric acid	7.34	1.0	5.0	"
4.	Zinc sulfate	158.53	1.0	1.0	Good
	Ferric sulfate	6.58			
	Sulfuric acid	7.34	1.0	5.0	"
	Citric acid	2.00			
	Glucose	2.00			
	Glue	1.00			
5.	Zinc sulfate	158.53	1.0	1.0	Very good
	Ferric sulfate	6.58			
	Sulfuric acid	7.34	1.0	5.0	" "
	Glucose	2.00			
	Glue	1.00			

Temperature 60° to 70° F. throughout.

Solution no. 1 very evidently had decidedly too much glue in it, for theglue settled out in large quantities, and during electrolysis there was an excessive amount of frothing. There was a slight evolution of gas from the anode -- more than in either solution no. 5 or the Meaker solution.

Solution no. 2 also showed some sediment and frothed badly, though there was not so much sediment nor so much frothing as in no. 1.

Solution no. 3 showed no sediment, nor did it froth during electrolysis. This would be expected, since it contained no addition agents.

Solutions 4 and 5 showed no more sediment, even on long standing, than the Meaker solution, though both frothed during electrolysis.

None of the baths except no. 2 showed any sign of failure and all the deposits, except that from solution no. 2 compared very favorably with that obtained from the Meaker solution. In fact, the deposits from nos. 1, 4, and 5, especially 5, were if anything, brighter than that from the Meaker solution. The plating was just as uniform, and of as good quality, after the 5 hr. run as after the first hour.

The results of electrolysis show that even one gram of glue per liter is more than is necessary to obtain a good coating of zinc. Whether the glucose has any beneficial result or not could not be judged from the solutions tested. However, it certainly has no harmful effect, as the addition of a comparatively large quantity of tartaric acid and dextrine to the glue and glucose together are beneficial, though correct proportion of each would have to be determined by experiment.

Whether the solutions tested would stand up in long usage was not determined. This can only be decided by operating the cell continuously until the solution failed.

Summary.

1. It was found that the Meaker zinc plating solution is a rather concentrated solution of zinc sulfate, containing a small quantity of iron (probably as an impurity), a small quantity of sulfuric acid, and a relatively large amount of organic matter, the nature of which has not been determined.

2. The effect of several addition agents was tested, in an electrolyte made up of the same concentration of zinc sulfate, ferric sulfate, and sulfuric acid, as the Meaker solution.

3. Three zinc-plating baths were found, which gave a deposit that compared favorably with the deposit obtained from the Meaker solution.

4. Whether these three solutions would stand up in continuous service for more than five hours, or whether they would give satisfactory deposits at higher current density, was not determined.

5. The question of whether the amounts of addition agents used in these three solutions were the most efficient quantities was not determined, though the indications are that smaller quantities could be used with as good effect.

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