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TECHNICAL REPORT

By

W. O. Crawford

January 1966

U. S. ARMY WEAPONS COMMAND

ROCK ISLAND ARSENAL

RESEARCH & ENGINEERING DIVISION

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DEVELOPMENT OF AN IMPROVED RINSE SOLUTION FOR PHOSPHATE COATINGS THROUGH ADDITION OF ORGANIC ACIDS

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Laboratory Branch

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ABSTRACT

This work was undertaken in order to improve the salt spray resistance capabilities of phosphate coatings through innovations in the post treatment of the phosphate coatings and specifically through improvements in the supplementary rinse solutions.

Various compounds, both organic and inorganic, were tested in solution, both by themselves and in combination with each other and with the existing chromic acid rinse solution, as possible rinses for phosphate coatings.

It was found that four different 1-4 and 1-5 dicarboxylic acids, when used in the proper concentration with the existing 0.6 gm/liter (0.08 oz./gal.) chromic acid rinse increased the salt spray life of a phosphate coating by at least one hour over the salt spray life of a coating treated in the standard 0.6 gm/l chromic acid rinse. These four acids are: citric acid, glutaric acid, maleic acid and succinic acid.

It was also found that one aromatic dicarboxylic acid tested, phthalic acid, had the same effect on the salt spray life as the above mentioned aliphatic acids.

FOREWORD

This work was authorized under DA Number 1CO-24401-A110. The problem title is "Supplementary Treatments For Plated And Conversion Coatings," under subtask title, "Protective and Packaging Materials," which is under project, "Materials For Army Weapons and Combat Mobility."

The part played by phosphate coatings in the Army corrosion prevention program is well known. This work will attempt to produce a post-phosphating rinse solution of superior quality which will increase the protective usefulness of phosphate coatings.

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PROBLEM

The aim of this work was to increase the salt spray resistance of phosphate coating systems through improvement of the post treatment operation by innovations in the chromic acid rinse solution.

BACKGROUND

It is generally known and accepted that a phosphate coating on metallic surfaces contains pores or pinholes which expose the basis metal; it is at these points in the coating where initial corrosion of a specimen starts.(1) Therefore, parts are often rinsed in dilute chromic acid solutions after phosphating. Rinsing in these chromic acid solutions have been found to aid in hindering this initial corrosion.(1,2)

In the field of chromic acid rinse solutions, work has been carried out by Eisler and Doss(3) using tagged chromic acid rinse solutions on heavy manganese and zinc based phosphate coatings to determine optimum chromic acid concentrations to be incorporated in the rinse solutions. Further work by Doss(4) using chromic acid rinse solutions indicated that specimens rinsed in the chromic acid solutions exhibited less corrosion after the salt spray test. Tests conducted by McHenry and Doss(5) showed that as the concentration of chromic acid in rinse solutions increased, the phosphate loss from the coatings also increased.

Some success had been demonstrated by other workers using citric acid solutions in both the pretreatment and post treatment of phosphate coatings.(7,8)

At the present time, MIL-HDBK-205 "Phosphatizing and Black Oxide Coating of Ferrous Metals" recommends that an 0.6 g/l (0.08 ounce per gallon) chromic acid solution be employed as a rinse solution for phosphate coatings. However, difficulty has been experienced upon occasion in obtaining coatings that will meet the minimum salt spray requirements when phosphating with the room temperature phosphating bath; even when employing the chromic acid rinse solutions. It was decided, therefore, to try to improve the quality of the rinse solution in order to thereby improve the corrosion resistant qualities of the phosphate coating systems on which the rinse solutions are used.

APPROACH AND RESULTS

The investigation was programmed to cover the following specific areas.

A testing of miscellaneous proprietary rinse solutions was carried out in order to see what other investigators in this area had found and how other rinse solutions effected the salt spray resistance capabilities of a phosphate coating.

Various inorganic and organic additives were screened in order to determine what general direction the bulk of the work should follow.

Based on the results of the screening tests, tests were carried out in order to find the optimum concentration of organic acids that could be used in combinations with the standard 0.6 gm/l chromic acid rinse solution.

Tests were then run to determine the optimum level of chromic acid to be used in the rinse solution.

Lastly tests were run to determine the stability of the rinse solution developed during this work.

Testing of Miscellaneous Proprietary Materials

In this portion of the testing program, a number of commercially available products were evaluated as shown in Table I. These products were labeled A, B and C. Product A seems to be a thermosetting plastic suspension in water, product B is a chromic acid type rinse and product C is a combination chromic acid-organic type rinse.

In these tests panels were phosphated in sets of four and rinsed in accordance with the instructions supplied by the companies unless indicated otherwise in Table I. The control referred to in Table I is the 0.6 grams per liter (0.08 oz/gal) chromic acid rinse described in MIL-HDBK-205. All of the panels were subjected to the salt spray test conforming to the test recommended in MIL-P-16232B "Phosphate Coatings, Heavy, Manganese or Zinc Base (For Ferrous Metals)."

It can be seen from the results given in Table I that, of the materials tested only C was as good as the control and B and A were inferior to the control.

TABLE I

COMPARATIVE SALT SPRAY RESISTANCE OF COMMERCIAL PRODUCTS

Group #	Set #	Product	Solution	Salt Spray Test In Hours Passed	Salt Spray Test In Hours Failed
I	1		Control	2	3
	2	A	A	1	2
	3	A	2 to 1 A + water	1	2
	4	A	1 to 1 A + water	1	2
	5		Control	2	3
II	1		Control	3	4
	2	B	B	2	3
	3		Control	3	4
III	1		Control	2	3
	2	C	C for 45 secs. and post cured at 200°F for 10 min.	2	3
	3		Control	2	3

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TABLE II

SALT SPRAY RESISTANCE AFFORDED BY TRIAL FORMULATIONS

Group No.	Set No.	Solution Component	Component Concentration	Rinse Time in Secs.	Rinse Temp. in Deg. F	Salt Spray Results in Hours	
						Passed	Failed
I	1	Chromic Acid	0.6 gm/l (.08 oz/gal)	30	160-165	2	3
	2	Chromic Acid Citric Acid	15.0 gms/l 10.0 gms/l	30	70-90	1	2
	3	Chromic Acid Citric Acid	15 gms/l 10 gms/l	30	160-165	2	3
	4	Chromic Acid	0.6 gm/l	30	160-165	2	3
II	1	Chromic Acid	0.6 gm/l	30	160-165	2	3
	2	Chromic Acid nickel carbonate	0.6 gm/l 2.0 gms/l	30	160-165	2	3
	3	Chromic Acid oxalic acid	15 gms/l 10 gms/l	30	80	2	3
	4	Chromic Acid oxalic acid	15 gms/l 10 gms/l	30	160-165	2	3
III	1	Chromic Acid	0.6 gm/l	30	160-165	2	3
	2	Chromic Acid Cobalt acetate	0.6 gm/l 4.9 gms/l	30	160-165	2	3
	3	Chromic Acid	0.6 gm/l	30	160-165	2	3
IV	1	"	"	"	"	3	4
	2	Citric Acid acetic acid	1.0 gm/l enough to lower pH to 2.6	"	70-90	0	
	3	Citric Acid acetic acid	5 gms/l enough to bring pH to 2.6	30	70-90	0	
	4	Chromic Acid	0.6 gm/l	30	160-165	3	4

TABLE II (Cont.)

SALT SPRAY RESISTANCE AFFORDED BY TRIAL FORMULATIONS

Group No.	Set No.	Solution Component	Component Concentration	Rinse Time in Secs.	Rinse Temp. in Deg. F	Salt Spray Results in Hours Passed	Salt Spray Results in Hours Failed
V	1	Chromic Acid	0.6 gm/l	30	160-165	2	3
	2	" succinic acid	" 1 g/l	30	70-90	2	3
	3	Chromic Acid succinic acid	0.6 gm/l 1 g/l	30	160-165	3	4
	4	Chromic Acid tartaric acid	0.6 gm/l 1 g/l	30	160-165	3	4
	5	Chromic Acid stannous pyrophosphate	0.6 gm/l 1 gm/l	30	160-165	0	
	6	Chromic Acid	0.6 gm/l	30	160-165	2	3
VI	1	Chromic Acid	0.6 gm/l	30	160-165	3	4
	2	Chromic Acid citric acid	0.6 gm/l 1 gm/l	30	160-165	4	5
	3	Chromic Acid glutaric acid	0.6 gm/l 1 g/l	30	160-165	4	5
	4	Chromic Acid Cobalt acetate	0.6 gm/l 1 g/l	30	160-165	2	3
	5	Chromic Acid Cobalt acetate	0.6 gm/l 1 gm/l	30	160-165	2	3
	6	Chromic Acid malic acid	0.6 gm/l 1 g/l	30	160-165	2	3
	7	Chromic Acid adipic acid	0.6 gm/l 1 g/l	30	160-165	2	3
	8	Chromic Acid	0.6 gm/l	30	160-165	2	3

TABLE III

EFFECT OF CONCENTRATION OF SALT SPRAY RESISTANCE

Group No.	Set No.	Variable Component	Concentration of Var. Component	Salt Spray Results in Hrs. Passed	Salt Spray Results in Hrs. Failed	Coating Weights in Mgs. Per Sq. Ft.
I	1	None		2	3	2870
	2	Succinic acid	1 gram/liter	3	4	3400
	3	" "	5 grams per liter	1	2	3520
	4	" "	10 " " "	0		3560
	5	None		2	3	2450
II	1	"		2	3	2960
	2	Tartaric acid	1 gram per liter	2	3	2960
	3	" "	5 " " "	0		2900
	4	" "	10 " " "	0		1800
	5	None		2	3	2900
III	1	None		5	6	2500
	2	Phthalic acid	1 gram per liter	6	7	2670
	3	" "	5 " " "	4	5	2690
	4	" "	10 " " "	3	4	2820
	5	None		5	6	2600
IV	1	None		2	3	1840
	2	Citric acid	1 gram per liter	3	4	1850
	3	" "	5 " " "	2	3	1930
	4	" "	10 " " "	0		2040
	5	None		2	3	1840
V	1	None		4	5	1630
	2	Glutaric acid	1 gram per liter	5	6	1680
	3	" "	5 grams per liter	4	5	2000
	4	" "	10 " " "	4	5	1730
	5	None		4	5	1560
VI	1	None		3	4	1420
	2	Maleic acid	1 gram per liter	4	5	1430
	3	" "	5 " " "	0		1450
	4	" "	10 " " "	0		1470
	5	None		3	4	1390

TABLE III (Cont.)

EFFECT OF CONCENTRATION OF SALT SPRAY RESISTANCE

Group No.	Set No.	Variable Component	Concentration of Var. Component	Salt Spray Results in Hrs. Passed	Salt Spray Results in Hrs. Failed	Coating Weights in Mgs. Per Sq. Ft.
VII						
	1	None		2	3	1400
	2	Glutaric acid	0.5 grams per liter	2	3	1580
	3	" "	1.0 " " "	3	4	1590
	4	" "	2.5 " " "	2	3	1630
	5	None		2	3	1510
VIII						
	1	None		2	3	1350
	2	Succinic acid	0.5 grams per liter	2	3	1240
	3	" "	1.0 " " "	3	4	1970
	4	" "	2.5 " " "	1	2	2050
	5	None		2	3	1340
IX						
	1	None		4	5	1660
	2	Phthalic acid	0.5 grams per liter	4	5	1780
	3	" "	1.0 " " "	5	6	1860
	4	" "	2.5 " " "	4	5	1900
	5	None		4	5	1660
X						
	1	None		5	6	2000
	2	Tartaric acid	0.5 grams per liter	3	4	2120
	3	" "	1.0 " " "	2	3	2150
	4	" "	2.5 " " "	1	2	2160
	5	None		5	6	1890
XI						
	1	None		2	3	2350
	2	Citric acid	0.5 grams per liter	2	3	2400
	3	" "	1.0 " " "	3	4	2510
	4	" "	2.5 " " "	2	3	2540
	5	None		2	3	2300

TABLE III (Cont.)

EFFECT OF CONCENTRATION OF SALT SPRAY RESISTANCE

Group No.	Set No.	Variable Component	Concentration of Var. Component	Salt Spray Results in Hrs. Passed	Salt Spray Results in Hrs. Failed	Coating Weights in Mgs. Per Sq. Ft.
XII	1	None		1	2	1670
	2	Maleic acid	0.5 grams per liter	1	2	1680
	3	" "	1.0 " " "	2	3	1720
	4	" "	2.5 " " "	1	2	1740
	5	None		1	2	1750
XIII	1	None		2	3	1600
	2	Adipic acid	0.5 grams per liter	2	3	1640
	3	" "	1.0 " " "	2	3	1760
	4	" "	2.5 " " "	2	3	1800
	5	None		2	3	1580

Once again the 0.08 oz/gal. 0.6 g/l chromic acid rinse was used as a control. As only the effect of the organic acids is being tested the other variables were canceled out during this test, that is the rinse time was 30 seconds for all sets, the rinse temperature was maintained at 160-165°F for all sets, and the second component in each rinse solution, chromic acid, was maintained at 0.6 gm/l. Each group of sets represents a different day of phosphating. A 0.6 gm/l chromic acid rinse control solution was run at the beginning and end of each group to assure that no breakdown of the phosphate coating solution took place during the day of the groups processing.

It can be seen from the results shown in Table III that a solution of citric, or maleic, or glutaric, or succinic, or phthalic acid at a concentration of one gram per liter in combination with chromic acid at a concentration of 0.6 gm/l will increase the salt spray life of a phosphated panel by one hour over a panel rinsed in the 0.6 gm/l chromic acid control solution, where the other factors of rinsing, time and temperature, are 30 seconds and 160-165°F respectively. Adipic and tartaric acids showed some promise in the screening tests, see Table II, but subsequent tests, Table III, using these acids did not equal the initial results, Table II. Table III shows that as the concentrations of organic acid in the rinse solution is raised there is an increase in the coating weights obtained on the panels.

Testing for Optimum Concentration of Chromic Acid

In the following tests, Table IV, the optimum level of chromic acid to use with the one gram per liter organic acid will be found. In these tests, the other variables, organic acid concentration, rinse time, and rinse temperature, were kept constant at 1 g/l, 30 seconds and, 160-165°F. Once again a 0.6 gm/l chromic acid control rinse was run at the beginning and the end of each group.

The tests outlined in Table IV show that as the concentration of chromic acid in the rinse solution increases the coating weights decrease and that there is a tendency toward shorter salt spray resistances. Therefore, the concentration of 0.6 gm/l seems to be the best concentration to use.

TABLE IV

EFFECT OF VARYING CHROMIC ACID CONCENTRATION

Group No. and Organic Acid Type	Set No.	Chromic Acid Concentration	Salt Spray Results in Hours		Coating Weights In Mgs. Per Sq. Ft.
			Passed	Failed	
I Adipic acid	1	0.6 gm/l (.08 oz/gal)	3	4	2460
	2	1 gm/liter	3	4	2230
	3	5 gms/liter	3	4	2180
	4	10 gms/liter	3	4	2190
	5	0.6 gm/l	3	4	2350
II Succinic acid	1	0.6 gm/l	2	3	1650
	2	0.5 gm/liter	3	4	1720
	3	1 gms/liter	3	4	1610
	4	2.5 gms/liter	1	2	1780
	5	0.6 gm/l	2	3	1700
III Phthalic acid	1	0.6 gm/l	3	4	1650
	2	0.5 gm/liter	4	5	1850
	3	1 gm/liter	4	5	1700
	4	2.5 gms/liter	2	3	1320
	5	0.6 gm/l	3	4	1630
IV Citric acid	1	0.6 gm/l	2	3	1830
	2	0.5 gm/liter	3	4	2240
	3	1.0 gm/liter	3	4	2210
	4	2.5 gms/liter	2	3	1920
	5	0.6 gm/l	2	3	1680
V Glutaric acid	1	0.6 gm/l	2	3	2600
	2	0.5 gm/liter	3	4	3000
	3	1.0 gm/liter	3	4	2760
	4	2.5 gms/liter	3	4	2660
	5	0.6 gm/l	2	3	2490
VI Maleic acid	1	0.6 gm/l	2	3	2300
	2	0.5 gms/liter	3	4	2460
	3	1.0 gm/liter	3	4	2660
	4	2.5 gms/liter	3	4	2170
	5	0.6 gm/l	2	3	2890

Stability Tests and Trivalent Chrome Analysis

In these tests, all of the organic-chromic acid rinse solutions that have been found superior to the 0.6 gm/l (0.08 oz/gal) control were prepared and used on three groups of panels on three different days, as the rinse solution production are prepared fresh every day this test proves that the new solutions are stable enough to use in production. In all the rinses the chromic acid concentration is 0.6 g/l, the organic acid concentration is 1 g/l, the rinse time is 30 secs., and the rinse temperature is 160-165°F. In all the previous tests each group was rinsed in fresh solutions.

The last two groups, II and III, of seven sets of panels were processed three days apart and rinsed in organic acid-chromic acid solutions that had been held over the three days. All of the other groups in all of the phases were rinsed in solutions that had been freshly prepared on the days that the groups were phosphated.

DISCUSSION

None of the inorganics initially tested produced any increase in the salt spray resistance qualities of the phosphate coatings so a detailed study of inorganic additives to rinse solutions was not carried out.

The organics tested in this work were, citric acid, succinic acid, maleic acid, glutaric acid, malic acid, tartaric acid, oxalic acid, acetic acid and phthalic acid. Of these, the first four and the last one mentioned had the effect of improving the salt spray resistance of phosphate coatings when the coatings were treated in solutions containing these organic acids in the proper concentrations in the existing 0.6 gm/l (0.08 oz/gal.) chromic acid rinse solution.

It can be seen from the results of the work described in this report; that five supplementary rinse solutions have been developed that will increase the salt spray resistance of a phosphate coating by at least one hour over the salt spray resistance of a phosphate coating treated with the 0.6 gm/l (0.08 oz/gal.) chromic acid rinse solution. The solutions are, a one gram per liter citric, 0.6 g/l chromic acid solution, a one gram per liter glutaric acid-0.6 g/l chromic acid solution, a one gram per liter maleic acid-0.6 g/l chromic acid solution, a one gram per liter succinic acid-0.6 g/l chromic acid solution, and a one gram per liter phthalic acid-0.6 g/l chromic acid solution.

TABLE V

EFFECT OF RINSE SOLUTION AGE ON SALT SPRAY RESISTANCE

Group No.	Set No.	Organic Acid	Salt Spray Results in Hours Passed	Failed	Coating Weights in Mgs. Per Sq. Ft.
I					
	1	None	2	3	1320
	2	Citric	3	4	1330
	3	Succinic	3	4	1330
	4	Glutaric	3	4	1570
	5	Maleic	3	4	1550
	6	Phthalic	3	4	1410
	7	None	2	3	1310
II					
	1	None	2	3	1240
	2	Citric	3	4	1920
	3	Succinic	3	4	2280
	4	Glutaric	3	4	1780
	5	Maleic	3	4	1600
	6	Phthalic	3	4	1400
	7	None	2	3	1190
III					
	1	None	2	3	1000
	2	Citric	3	4	1180
	3	Succinic	3	4	1330
	4	Glutaric	3	4	1190
	5	Maleic	3	4	1300
	6	Phthalic	3	4	1240
	7	None	2	3	1060

On considering the possible explanations of the mechanisms by which the addition of such a small amount of organic acid to the standard 0.6 gm/l chromic acid rinse solution could increase the salt spray resistance of a phosphated panel treated in the solution by an additional hour over the salt spray resistance of panels treated in the standard solution; three possibilities arise.

Based on the Baeyer strain theory,(9,10) the carboxyl groups of the four aliphatic acids found to be effective in the supplementary rinse solutions are in close proximity to one another; this fact indicates that there is a relatively strong partial negative charge present in the vicinity of these carboxyl groups. By the same Baeyer strain theory, the carbon atom in each of the aliphatic acids form a loop. It is possible that, when the freshly phosphated panels are rinsed in the solutions containing the organic acids, the partial negative charge around the two closely oriented carboxyl groups is attracted to a positive charge present on the phosphate crystal lattice and attaches the organic acid loosely to the surface of the phosphate coating by much the same mechanism as the various organic inhibitors used in steel pickling solutions.(11) If this reaction does take place, then the loop of carbon atoms would undoubtedly cover some of the pinholes in the phosphate coating where initial corrosion of the phosphated piece takes place. In the case of the aromatic acid found to be of value in the rinse solutions. The same theory would apply, except for the fact that there is no need to use the Baeyer strain theory as the carbon atoms in phthalic acid are actually present in a ring formation. The above tentative explanation of the mechanism by which the organic acids used enhance the salt spray resistance of a phosphate coating would seem to be the most logical one.

There is another possible explanation that can be put forward as to the increased salt spray resistance of coatings treated with the organic acid-chromic acid rinse solutions over coatings treated with the standard chromic acid rinse solution. The theory of trivalent chromium precipitation on coatings(1,2) is that trivalent chromium is attracted to weak and/or bare spots in the coatings, precipitate on the weak spots, and set up a partial barrier at the aforesaid weak spots.(2) As the organic acids used are capable of forming complexes with metal ions,(12) it is possible that the organic acids form complexes with the trivalent chromium ions present in the solution, and in this way facilitate the transfer of the trivalent chromium ions from the solution to the phosphate coating; thus giving a greater density of trivalent chromium ions on the weak spots in the coating.

A third possible explanation of the improved salt spray resistance of the panels treated in the organic acid-chromic acid rinse solutions, is that phosphate coatings are not smooth but consist of peaks and valleys or high and low spots. It is possible that the organic acids, which have low ionization constants and are not highly polar settle in the low spots on the phosphate coatings whereas the highly ionic and polar chromic acid attacks the high spots setting up an active passive differential in the same manner as in a solution of oxalic acid and sulfuric acid that is used in tumble deburring.(13) This phenomenon of having an organic acid coating protecting the low, or thin, spots on the coating while the panel is immersed in the rinse solution would prevent etching of the low spots of the coating thus increasing the salt spray resistance of the coatings.

All of the three theories mentioned above would also tend to explain the increase in coating weights obtained when using the chromic acid-organic acid rinse solutions rather than the standard chromic acid rinse solutions.

A logical explanation as to why a concentration of 0.1 per cent of the organic acids used increases the salt spray resistance of the phosphate coatings when used in the chromic acid rinse solutions while concentrations of 0.25% and above seem to be detrimental to the salt spray resistance capabilities of the coatings is that the organic acids used are oxidizable,(9) and in the presence of the strong oxidizing agent, chromic acid, the advantageous effect gained by the presence of a small amount of the organic acid in the solution is offset when enough organic acid is added to reduce an appreciable amount of the chromic acid present.

There would appear to be no problems involved in the use of the organic acids in a shop production situation. There are several chemical companies that produce citric acid and/or maleic acid and/or succinic acid on a commercial basis at a reasonable price. Maintenance of the level of organic acid concentration needed in the rinse solution would be no problem as the rinse solution is discarded and a fresh solution prepared every day.(18) The phase four tests showed that the solutions developed are stable for at least three days.

CONCLUSIONS

It can be seen that the organic acid-chromic acid rinse solutions developed are superior to the 0.6 gm/l chromic acid rinse solution recommended for use with phosphate coatings by MIL-HDBK-205.

In the phase two tests, in every case, the solutions containing the five organic acids found to be beneficial to the rinse solutions showed the following characteristic. As the concentration of organic acid in the rinse solution was increased the coating weights obtained increased. However, only at the concentration of one gram per liter did the organic acids show any tendency to increase the salt spray resistance capabilities of the phosphate coatings. At the one gram per liter concentration of organic acid the salt spray resistance capabilities of the phosphate coatings treated were increased to the point where each coating treated lasted one hour longer than the coatings treated with the 0.6 gm/l rinse solution; this was true in all of the tests in all of the phases.

The concentration of chromic acid that should be used in combination with the one gram per liter organic acid is 0.6 gm/l chromic acid. The phase three tests showed that at concentrations significantly higher than this the salt spray resistant capabilities of the phosphate coatings treated are decreased rather than increased.

RECOMMENDATIONS

It is recommended that one of the following organic acids, citric, succinic, glutaric, maleic, or phthalic, be in corporated into the 0.6 gm/l chromic acid rinse solution at an installation and compared with the standard rinse solution in use at the same installation on phosphated work processed at the installation in order to verify the results obtained from the tests described in this report.

After the above pilot tests are completed, and the conclusions drawn in this report verified as sound when applied to shop procedures and practices; it is recommended that the addition of the organic acids tested be incorporated into the existing 0.6 gm/l chromic acid rinse solution recommended in MIL-HDBK-205 at a level of one gram per liter of solution.

LITERATURE CITED

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