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A METHOD OF PROTECTING METAL
POWDERS FROM DETERIORATION

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18 April 1951



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Date-16 Feb 1956 *W. H. H. H. H.*
By direction of Chief, Bureau
of Ordnance

U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

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A METHOD OF PROTECTING METAL POWDERS FROM
DETERIORATION

Prepared by:

R. H. Comyn and R. Skelton

ABSTRACT: A method has been developed for protecting manganese and cobalt powders from deterioration in order to improve the surveillance qualities of gasless delay mixtures which use these powders as fuels. The protection is provided by treating the surface of the metal powder first with a hot aqueous potassium dichromate solution and then with a solution of stearic acid in carbon tetrachloride. The resulting surface coating improves the resistance of the metal powder to corrosion at 160°F., and 95% relative humidity. The stearic acid treatment adds about 1×10^{-7} grams of carbon per cm^2 of the metal powder surface. This addition appears to be uniform. Gasless delay mixtures which utilize either of these treated metal powders as fuels have satisfactory burning and storage qualities.

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18 April 1951

The investigations outlined in this report form a part of the general investigation, Development of Gasless Fuze Powder, Task NOL-Re2c-104-2-51. The report is based on experimental work conducted by the Chemistry Division of the Engineering Department of the Naval Ordnance Laboratory and, as such, may be of interest to other activities engaged in similar investigations.

W. G. SCHINDLER
Rear Admiral, USN
Commander

S. W. Booth
By direction

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A METHOD OF PROTECTING METAL POWDERS FROM
DETERIORATION

INTRODUCTION

1. The use of either cobalt powder or manganese powder as a fuel in gasless delay mixtures is described in reference (a). Since it is desirable for gasless mixtures to withstand high humidity at temperatures up to 160°F. without deterioration, the ability of these two fuels, cobalt and manganese, to withstand decomposition in hot humid atmospheres is important. Since preliminary tests indicated that both of these powders deteriorated rapidly under these conditions, this study was made in order to determine the most effective method of inhibiting this decomposition. The subsequent use of these powders in gasless delay compositions prevented the use of such materials as wax or varnish as a protective coating. It would be necessary to use a large excess of such materials to protect the metal powders, which would lead to excessive gas formation in the presence of the oxidizing agents in gasless mixtures and also lead to non-reproducible burning rates.

TEST CONDITIONS

2. It was decided that the weight increase of the metal powders, after exposure to a warm humid atmosphere, would be used as a measure of the deterioration of the metal. About 2 gm. of the metal powder was placed in a tared, 50 cc. beaker. The beaker and its contents were dried one hour at 71°C. (160°F), and allowed to cool in a desiccator. Since a number of samples was tested at one time, it was believed that the necessary repeated opening of the desiccator would lead to erratic sample weights, and, therefore, after cooling, the beaker and its contents were allowed to stand in the open air for 15 minutes in order to come to equilibrium with room conditions. The beaker and its contents were then weighed and placed in a desiccator over a saturated solution of potassium sulfate and held at 71°C. $\pm$ 1°C. (160°F). The potassium sulfate solution was used to hold the relative humidity at 95% (reference b). After the same had been exposed to the warm humid air for a definite time interval, it was removed and dried for one hour at 71°C. ambient humidity, and cooled and weighed as described above.

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PROTECTIVE COATINGS FOR COBALT POWDERS

Potassium Dichromate Treatments

3. The use of potassium dichromate treatment for protecting metal powders from subsequent deterioration is reported in reference (c). This method was followed, using the procedure outlined in Appendix I, Treatment A. The corrosion tests on two lots of cobalt powder treated in this manner are compared with corrosion tests on the same lots of untreated cobalt, in Table I, Test Nos. 1 and 2. These results indicate that the corrosion of cobalt powder may be partly inhibited by this treatment, but the corrosion rate is still high enough to eliminate this method of corrosion inhibition.

Effect of Washing Cobalt Prior to Dichromate Treatment

4. In order to determine the effect of cleaning the surface of the cobalt prior to treating the surface with potassium dichromate, the cobalt powder was stirred in a water solution of the commercial detergent "Dreft" as described in Appendix I, Treatment D. It was found that the Dreft solution was very difficult to filter, and therefore, a centrifuge was used to separate the cobalt from the Dreft solution as well as to wash the cobalt in subsequent dichromate treatments. After the cobalt powder was washed as described in Appendix I, Treatment D, it was treated with potassium dichromate, Appendix I, Treatment C. As a comparison, cobalt powder was also treated directly with potassium dichromate, as described in Appendix I, Treatment C. The corrosion tests shown in Table I, Test Nos. 3 and 4, indicate that this washing of cobalt powder prior to dichromating has little effect on its resistance to corrosion.

Stearic Acid Treatments

5. It is assumed that the initial step in the corrosion of metals in a warm humid atmosphere involves the condensation of a water film on the metal surface (reference d). The use of a coating of a long chain aliphatic acid to protect the metal from this water film condensation has been studied and is reported in several papers (references e, f, and g). It is assumed that the acidic end of the organic molecule is attracted toward the metal surface, leaving the aliphatic part of the molecule turned outward. Since the aliphatic ends of the long chain acids are hydrophobic, the metal is effectively waterproofed, and the condensation of water on the metallic surface is prevented. Reference f, reports

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that up to a certain point the amount of aliphatic acid absorbed on metal surfaces is independent of the concentration of the acid in the contact solution and cannot be removed by washing with solvents. Beyond that point the amount absorbed varies directly with concentration and the excess can be removed by washing with solvents. Since the metal powders are to be used in delay mixtures in which minimum gas formation and reproducible burning rates are important, it was decided to wash the metal powder thoroughly after the organic acid had been adsorbed in order to keep the amount of adsorbed acid at a reproducible minimum. Since stearic acid is a readily available long chain saturated aliphatic acid, it was used to provide the protective coating.

Stearic Acid Treatment on Untreated Cobalt

6. Two lots of cobalt powder were treated with stearic acid according to the instructions outlined in Appendix I, Treatment B. The fact that the stearic acid adhered to the metal powder was shown by the fact that the treated powder could not be dispersed readily in a beaker of water but either floated on top of the water or sank in a globule of powder to the bottom of the beaker. However, the results of the corrosion tests on these samples shown in Table I, Test No. 5, indicate that the stearic acid treatment alone does not inhibit the corrosion of cobalt powder to any great extent.

Stearic Acid Treatment on Dichromated Cobalt

7. Two lots of cobalt powder which had previously been treated by potassium dichromate, Appendix I, Treatment A, were treated with stearic acid, Appendix I, Treatment B. The results of the corrosion test, Table I, Test No. 6, show that the rate of deterioration of cobalt powder treated in this manner is slow enough so that the powder may be considered to be adequately protected. Further tests were run in which the cobalt was washed using a centrifuge to aid decantation, after both the dichromate and stearic acid treatments. (Appendix I, Dichromate Treatment C, and Stearic Acid Treatment E). An additional test was run in which the cobalt was washed in a solution of Dreft, (Dreft Wash Treatment D), prior to treating with dichromate and stearic acid solutions. The results of corrosion tests on both of these samples are shown in Table I, Test Nos. 7 and 8. The corrosion resistance of these samples compares closely with the corrosion resistance of the samples shown in Table I, Test No. 6, and there does not appear to be any advantage in using the preliminary Dreft wash.

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PROTECTIVE COATINGS FOR MANGANESE POWDER

Potassium Dichromate Treatments Without Potassium Acid Sulfate

8. If manganese powder is added to a solution of potassium dichromate and potassium acid sulfate, Dichromate Treatment A, Appendix I, a noticeable reaction occurs between the potassium acid sulfate and the manganese. This reaction is sufficiently violent to necessitate adding the manganese very slowly. As a result, the potassium acid sulfate is depleted before the bulk of the manganese is added to the solution and the treatment of the whole sample is not consistent. Therefore, tests were made to determine the practicability of treating the manganese with a potassium dichromate solution without using potassium acid sulfate. It was also desirable to determine the effect of washing the manganese, prior to the dichromate treatment, with the commercial detergent "Dreft". Since this latter treatment necessitated the use of a centrifuge, paragraph 4, tests were run to determine whether the corrosion resistance of the treated powder was affected by the method of washing after the dichromate treatment. Two lots of manganese powder were treated by Dichromate Treatment A, Appendix I, in which the manganese was washed with distilled water on a suction filter; by Dichromate Treatment C, Appendix I, in which a centrifuge was used to facilitate the washing after treatment; and by Dreft wash Treatment D, Appendix I, followed by Dichromate Treatment C. The potassium acid sulfate was omitted from these dichromate treatments. The corrosion tests on samples of manganese powder treated by these methods are compared with tests on untreated samples in Table II, Test Nos. 1, 2, 3 and 4. The results indicate that the corrosion inhibition furnished by these treatments is not sufficient to justify their use.

Potassium Dichromate Treatments Using Potassium Acid Sulfate

9. In order to determine the effect of potassium acid sulfate on the dichromating of manganese, two lots of manganese were treated by Dichromate Treatment F. In this method, the manganese was added to the hot dichromate solution, and a second solution of .272 gm of potassium acid sulfate in 100 cc. of distilled water was added slowly over a 15 minute period while stirring at 95°C. It was believed that by this method, the whole of the manganese sample would receive equal treatment. The results of corrosion tests on samples treated in this manner are compared with corrosion tests on samples of untreated manganese powder, in Table III, Test Nos. 1 and 2. The number of water washes after the dichromate treatment was varied as shown in Table III, Test No. 2. The tests indicate that the addition of potassium acid sulfate during the

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dichromate treatment improves the corrosion resistance of manganese powder. The effect of additional washing after the dichromate treatment is inconclusive. The tests were terminated after 20 days of exposure due to lack of oven space. However, other tests which will be discussed in later paragraphs, indicated that other methods of treatment would be superior to this method.

STEARIC ACID TREATMENTS

Stearic Acid Treatment on Untreated Manganese

10. Two lots of manganese powder were treated with stearic acid according to the method outlined in Appendix I, Treatment B. As in the case of the cobalt powder treated in the same manner, the treated manganese appeared to be water resistant. However, the results of the corrosion tests on these samples, shown in Table II, Test No. 5, indicate that the stearic acid treatment alone does not inhibit the corrosion of manganese powder to any great extent.

Effect of Pretreating Manganese Prior to Stearic Acid Treatment

11. Various methods of treating manganese with potassium dichromate were used to determine the effect on subsequent stearic acid treatments. Two lots of manganese powder, which previously had been treated by potassium dichromate, Appendix I, Treatment A, without the addition of potassium acid sulfate (paragraph 8) were treated with stearic acid, Appendix I, Treatment B. Further tests were run on manganese, which had been subjected to the Dreft wash Treatment D, followed by Dichromate Treatment C, and finally by Stearic Acid Treatment E. The results of the corrosion tests on these samples, shown in Table II, Test Nos. 5, 6, 7, and 8, indicate that the latter treatment, involving the Dreft wash prior to the dichromate and stearic acid treatments, appears to best inhibit the corrosion of the manganese. However, the commercial detergent "Dreft" is not made according to a fixed formula and in fact, the composition has recently been changed by the manufacturers. Therefore, a change was made in the dichromate procedure in an attempt to obtain satisfactory inhibition after the final stearic acid treatment without using the initial Dreft wash. A series of tests were made on samples of manganese which had been treated by Dichromate Treatment F, followed by Stearic Acid Treatment G. The quantity of potassium acid sulfate, as well as the concentration of the potassium acid sulfate solution added during the dichromate treatment prior to the stearic acid treatment, were varied as shown in Table IV, as well as the number of washes with distilled water after dichromating. The results appear to indicate that 0.272 gm. of potassium sulfate, added during the initial dichromating, is

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preferable to .010 gm of the same material and that the lower concentration of potassium acid sulfate, .272 gm/100 cc, is preferable to the higher concentration of .272 gm/15 cc. The data on the effect of the number of water washes after the dichromate treatment, prior to the stearic acid treatment is somewhat erratic but it appears that a low number of washes is preferable.

EFFECT OF SURFACE TREATMENT OF FUELS ON THEIR USE IN
GASLESS DELAY COMPOSITIONS

12. Full data are not available on the effect of the surface treatment of manganese and cobalt powders on their subsequent use in gasless delay compositions. In general, the surface treatment of the fuels appears to tend to increase slightly the burning rate of gasless delay mixtures in which they are used. However, tests on delay mixtures in which the fuel is treated with both the dichromate and stearic acid treatments (reference h) indicate that there is no excessive gas formation, that the mixtures burn satisfactorily, and that there is a definite improvement in surveillance qualities.

IMPURITIES ADDED TO METAL POWDERS BY SURFACE TREATMENT

13. Preliminary tests on cobalt powder treated by Dichromate Treatment A, indicate that as much as 1 or 2% chromium may be added to the surface of the cobalt. No data are available on manganese powder treated with potassium dichromate. However, delay mixtures using fuels treated with potassium dichromate and the subsequent stearic acid treatment appear to have reproducible burning rates and the addition of the chromium to the surface of the fuel does not have any adverse effect on the performance of the delay mixtures. The effect of any large addition of stearic acid may become more serious in view of the potential gas which may be found by reaction between the stearic acid and the oxidizing agents in the delay mixtures. Carbon analyses were made on samples of cobalt and manganese powder after the dichromate treatments, and again after the combined dichromate and stearic acid treatments. The particle size distribution of the cobalt and manganese powders is shown in Table V, and the carbon analyses in Table VI. Only one set of carbon analyses was obtained on the cobalt samples but the results indicate that the carbon increase resulting from the stearic acid coating is only a small percentage of the carbon already in the cobalt and should cause no trouble. Carbon analyses for two lots of manganese are shown in Table VI. The Roller analyses of these two lots of manganese, Table V, show that the particle size distributions, and therefore presumably the surface areas are very nearly equal. Since the quantity of stearic acid added to the surface of a metal powder by the treatment probably depends on the surface

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area of the powder, it would be expected that a uniform coating procedure would result in an equal addition of stearic acid to each of these two lots of manganese. The results of the carbon analyses in Table VI indicate that equal amounts of carbon, and therefore stearic acid, are added to samples of the two lots of manganese. The maximum stearic acid that can be added to the manganese powder, Lot 2007 is given by the following equation, assuming that the stearic acid is present in a monomolecular film:

$$W = \frac{(A_{mn}) (N)}{(A_{st}) (N)}$$

W = gm of stearic acid adsorbed in complete monolayer on one gram of Lot 2007 manganese powder.

A_{mn} = 1985 cm²/gm. surface area of Lot 2007 manganese as determined by the nitrogen adsorption method.

N = 284.5 gm. Gram-molecular weight of stearic acid

A_{st} = 22×10^{-16} cm² cross sectional area of stearic acid molecule (reference 1)

N = Avogadro's number 6.06×10^{23} molecules/gm-mol.

$$W = \frac{1985 \times 284.5}{22 \times 10^{-16} \times 6.06 \times 10^{23}} = 424 \times 10^{-6} \text{ gram of stearic acid adsorbed in complete monolayer on one gram of Lot 2007 manganese powder}$$

14. The stearic acid actually adsorbed on one gram of manganese powder can be calculated from the carbon analysis of the coated powder by the following formula:

$$W_{st} = (W_{c2} - W_{c1}) \frac{M_{st}}{M_c}$$

W_{st} = grams stearic adsorbed on one gram of manganese

W_{c2} = .00034 grams of carbon per gram of manganese after adsorption of stearic acid

W_{c1} = .00010 grams of carbon per gram of manganese before adsorption of stearic acid

M_{st} = 284.5 gm. Gram-molecular weight of stearic acid

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Mc= 216 gm. Weight of carbon in one mol of stearic acid

Wst= $.00025 \times \frac{284.5}{216} = 329 \times 10^{-6}$ grams of stearic acid
adsorbed on one gram of Lot
2007 manganese powder

15. Although these results indicate that there may not be sufficient stearic acid adsorbed on the manganese to cover it completely with a monomolecular layer, there is no evidence to show whether the stearic acid is spread out over part of the manganese in a monomolecular layer or whether it is collected on smaller portions of the surface in layers several molecules thick.

CONCLUSIONS

16. The atmospheric corrosion of cobalt and manganese powders at 95% relative humidity, and 160°F. can be inhibited by a dichromate treatment followed by a stearic acid treatment.

17. The corrosion inhibition of either cobalt or manganese obtained by the combined dichromate-stearic acid treatments is superior to the inhibition obtained by either treatment alone.

18. The quantity of stearic acid adsorbed by the metal powder during the treatment appears to be constant for a given sample of metal powder and is about 2×10^{-4} gm of stearic acid per gram of metal powder whose surface area is 2000 cm² per gram.

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Table I

Corrosion Tests on Treated Samples of Cobalt Powder

Test No.	Treatment	Lot No.	% Weight Increase of Sample After Exposure at 160°F, 95% RH					
			Days Exposure					
			12	24	36	47	59	69
1	None	1735	8.96	11.30				
		1081	3.32	4.54				
2	Dichromate Treatment A	1735	0.45	0.50	1.15			
		1081	1.50	2.52				
3	Dichromate Treatment C	1735	0.43	0.59	2.48			
4	Dreft Wash Treatment D followed by Dichromate Treatment C	1735	0.59	1.00	1.62			
5	Stearic Acid Treatment E	1735	1.95	4.80				
		1081	0.83	1.21				
6	Dichromate Treatment A followed by Stearic Acid Treatment E	1735	0.31	0.40	0.44*			
		1081	0.24	0.31	0.34	0.34	0.35	0.40
7	Dichromate Treatment C followed by Stearic Acid Treatment E	1735	0.32	0.40	0.45*			
8	Dreft Wash Treatment D followed by Dichromate Treatment C followed by Stearic Acid Treatment E	1735	0.30	0.37	0.45*			

* Test Stopped due to lack of oven space.

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Table II

Corrosion Tests on Treated Samples of Manganese Powder

Test No.	Treatment	Lot No. of Manganese	% Weight Increase of Sample After Exposure at 150°F 95% RH			
			12	24	36	75
				days exposure		
1	None	2006	3.25	5.24	=====	
		1692	5.98	8.20	=====	
2	*Dichromate Treatment A	2006	0.88	1.60	=====	
		1692	1.00	2.63	=====	
3	*Dichromate Treatment C	2006	0.65	1.72	=====	
		1692	0.89	2.20	=====	
4	Droft Wash Treatment D followed by Dichromate Treatment C	2006	1.00	1.92	=====	
		1692	1.36	2.68	=====	
5	Stearic Acid Treatment B	2006	1.21	3.75	=====	
		1692	1.00	2.63	=====	
6	Dichromate Treatment A followed by Stearic Acid Treatment B	2006	0.10	0.29	0.90	=====
		1692	0.15	0.88	3.36	=====
7	Dichromate Treatment C followed by Stearic Acid Treatment E	2006	0.10	0.40	1.27	=====
		1692	0.15	0.77	2.89	=====
8	Droft Wash Treatment D followed by Dichromate Treatment C, followed by Stearic Acid Treatment E	2006	0.15	0.18	0.26	0.82
		1692	0.09	0.16	0.45	3.68

* No KHSO_4 used in Dichromate Treatment A&C of powdered manganese.

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Table III

Test No.	Treatment	Lot. No.	No. of washes after dichromating	% Weight Increase of Sample After Exposure at 160°F, 95% RH						
				Days Exposure						
				10	20	30	40	50	60	70
1	None	2007	-----	2.45	-----	-----	-----	-----	-----	-----
		2008	-----	1.97	-----	-----	-----	-----	-----	-----
2	Dichromate Treatment F .272 gm KHSO_4 in 100cc distilled water added during first 15 min. of dichromate treatment	2007	2	0.20	0.48**	-----	-----	-----	-----	-----
		2008	2	0.22	0.63**	-----	-----	-----	-----	-----
		2007	12	0.33	0.83**	-----	-----	-----	-----	-----
		2008	12	0.26	0.63**	-----	-----	-----	-----	-----
3	Dichromate Treatment F (.277 gm KHSO_4 in 100cc distilled water added) followed by Stearic Acid Treatment 6	2007	2	.05	.09	.17	.29	.47	.84	1.24
		2008	2	.05	.09	.17	.25	.40	.70	---
		2007	12	.04	.08	.22	.52	1.10	2.39	---
		2008	12	.03	.07	.11	.19	.32	.79	---

* 25cc of distilled water at 25°C used for each wash.

** Tests terminated due to lack of oven space

Table IV

Column	Treatment	Lot. No.	No. of Washes ^a After Dichromating	% Weight Increase of Sample After Exposure at 1600r, 95% RH						
				Days Exposure						
				10	20	30	40	50	60	70
1	Dichromate Treatment F 2007 followed by Sulfuric Acid 2007 Treatment G .872 gm KHSO ₄ 2008 in 100cc distilled water 2008 added during dichromating		2	.05	.09	.17	.29	.47	.84	1.24
			12	.04	.08	.22	.52	1.10	2.19	---
			2	.05	.09	.17	.25	.40	.70**	---
			12	.03	.07	.11	.19	.32	.79**	---
2	Dichromate Treatment F 2007 followed by Sulfuric Acid 2007 Treatment G .872 gm KHSO ₄ 2008 in 45cc distilled water 2008 added during dichromating		2	.04	.14	.27	.54	.99**	---	---
			12	.04	.14	.26	.48	.93**	---	---
			2	.04	.12	.40	.65	1.20	---	---
			12	.06	.20	.36	.49	.84**	---	---
3	Dichromate Treatment F 2007 followed by Sulfuric Acid 2007 Treatment G .610 gm KHSO ₄ 2008 in 100cc. distilled water 2008 added during dichromating		2	.06	.18	.52**	---	---	---	---
			12	.17	.37**	---	---	---	---	---
			2	.10	.23**	---	---	---	---	---
			12	.07	.19**	---	---	---	---	---

^a 25cc of distilled water at 25°C used for each wash.
Test cancelled because of lack of oven space

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Table V

Particle Size Distribution of Manganese and Cobalt Powder
Used in Surface Treatment Tests

Metal	Lot No.	Screen Analysis		Roller Analysis-Weight Percent				Surface Area by Nitrogen Adsorption cm^2/gm
		-325 Mesh	+325 Mesh	0-5 Micron	5-10 Micron	10-20 Micron	20-40 Micron	
Cobalt*	1081	99.8	0.2	----	----	----	----	----
Cobalt*	1735	99.8	0.2	19.8	20.1	22.5	37.6	----
Manganese*	1692	99.9	0.1	----	----	----	----	----
Manganese*	2006	99.8	0.2	10.0	18.7	33.6	36.9	----
Manganese*	2007	99.9	0.1	10.5	24.9	43.9	19.7	1985
Manganese*	2008	99.8	0.2	10.4	24.2	43.5	21.3	----

*Obtained from Metals Disintegrating Co. Elizabeth, N.J.

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Table VI

Carbon Analyses of Treated and Untreated Samples of Manganese and Cobalt

Metal	Lot No.	Treatment	Carbon Analysis % Carbon	Treatment	Carbon Analysis % Carbon	Increase in Carbon due to stearic acid Treatment
			Individual Determination		Individual Average Determination	
Cobalt	1735	Dichromate Treatment A	0.109	Stearic Acid Treatment B Pretreated by Dichromate Treatment A	0.112	0.017
			0.106		0.136	
			0.108		0.126	
Manganese	2007	Dichromate Treatment F	0.009	Stearic Acid Treatment E Pretreated by Dichromate Treatment F	0.037	0.024
			0.011		0.031	
			0.010			
			0.005			
Manganese	2008	Dichromate Treatment F	0.009	Stearic Acid Treatment E Pretreated by Dichromate Treatment F	0.036	0.025
			0.005		0.028	
			0.010			
			0.005			

* Carbon determinations furnished by Magnetic Materials Division

** .272 KPSO₄/100ccH₂O added during Dichromate Treatment F, and 2-25cc H₂O washes used after dichromating.

APPENDIX I

SURFACE TREATMENTS USED ON MANGANESE AND COBALT POWDERS

Treatment A: Dichromate Treatment

50 gm of the metal powder was added slowly with stirring, to a solution of 6.25 gm of $K_2Cr_2O_7$ and 0.63 gm. $KHSO_4$ in 125 cc. of distilled water at 95°C. After the metal powder was stirred 1/2 hr. at 95°C. it was filtered by suction and washed 20 times with 25 cc. portions of distilled water. The washed sample was dried 2 hrs. at 71°C.

Treatment B: Stearic Acid Treatment

50 gm of the metal powder was stirred 1 hr. in a solution of 6.25 gm. of stearic acid in 125 cc. of C. P. CCl_4 , at room temperature. The powder was filtered by suction and washed 10 times with 25 cc. portions of C. P. CCl_4 . The washed sample was dried 1 hr. at 71°C.

Treatment C: Dichromate Treatment - Modified

50 gm. of the metal powder was added slowly, with stirring, to a solution of 6.25 gm. of $K_2Cr_2O_7$ and 0.63 gm. $KHSO_4$ in 125 cc. of distilled water at 95°C. After the powder was stirred 1/2 hr. at 95°C., it was centrifuged and washed twice by decantation with 50 cc. of distilled water. The washed sample was dried 2 hrs. at 71°C.

Treatment D: Dreft Wash

50 gm. of metal powder was added, with stirring, to a solution of 0.13 gm. of the commercial detergent, "Dreft" in 125 cc. of distilled water, at room temperature. After the sample had been stirred 1/2 hr. it was centrifuged and decanted. The wet sample was then placed directly in the dichromating solution described in Treatment C.

Treatment E: Modified Stearic Acid Treatment

50 gm. of the metal powder was stirred 1 hr. in a solution of 6.25 gm. of stearic acid in 125 cc. of C. P. CCl_4 at room temperature. The powder was centrifuged and washed six times by decantation with 50 cc. portions of C. P. CCl_4 . The washed powder was dried 1 hr. at 71°C.

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APPENDIX I (continued)

Treatment F: Dichromate Treatment - Second modification

50 gm. of the metal powder was added slowly to a solution of 18.8 gm. of $K_2Cr_2O_7$ in 125 cc. of distilled water at 95°C. As soon as the addition of the metal powder was completed, a solution of $KHSO_4$ in distilled water at 25°C. was added slowly over a period of 15 minutes while the suspension was stirred at 95°C. The concentration and quantity of the $KHSO_4$ solution used are detailed in Tables III and IV. The metal powder was filtered with suction and washed with distilled water at 25°C. The washing procedure is also detailed in Tables III and IV. The washed sample was dried 2 hrs. at 71°C.

Treatment G: Stearic Acid Treatment - Second modification

50 gm. of the metal powder was stirred 1 hr. in a solution of 6.25 gm. of stearic acid in 125 cc. of C. P. CCl_4 . The powder was filtered and washed 4 times with 25 cc. portions of C. P. CCl_4 and then dried 1 hr. at 71°C.

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