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AFRPL-TR-66-262

Storable Concentrated Hydrogen Peroxide

Sponsoring Agency:
Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards, California
Air Force Systems Command, United States Air Force

Contract No. AF 04(611)-11416

Quarterly Progress Report No. 2
June - August, 1966

SHELL DEVELOPMENT COMPANY
A DIVISION OF SHELL OIL COMPANY
Emeryville, California

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Date of Issue: October 1966

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A Division of Shell Oil Company
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FOREWORD

This report describes research being carried out to improve the storability of concentrated hydrogen peroxide. The work is being conducted for the Air Force under Contract No. AF 04(611)-11416, Project No. 3148, BPSN 623148. The contract project officer is 1/Lt Ralph Fargnoli, USAF, Air Force Rocket Propulsion Laboratory, RPCL, Edwards, California. This Quarterly Report No. 2 describes the work carried out by Shell Development Company, Emeryville, California in the period June 1 to August 31, 1966.

Publication of this report does not constitute Air Force approval of the report's findings of conclusions. It is published only for the exchange and stimulation of ideas.

W.H.Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

Investigation of means for reducing the rate of decomposition of concentrated HP by removing the catalytic elements carried in the HP and by reducing the catalytic activity of the various materials of construction for use as containers has been continued.

For aluminum alloys various chemical treatments have not surpassed the caustic-nitric acid - hot concentrated HP sequence in achieving minimum surface activity. For stainless steel alloys only minor changes in surface activity have been achieved by chemical pretreatment. For both types of alloys the chemical composition is a primary factor governing surface activity.

Various combinations of inorganic ion-exchange media have not proved to be more effective than β-stannic acid alone in reducing the decomposition rate of the treated HP. Evaluation of HP-90 which had been treated by a β-stannic acid bed and stored in aluminum for approximately 1 year showed the HP to have about 1/3 the decomposition rate of the untreated feedstock.

Activities of tin surfaces electroplated onto aluminum have been shown to be several times higher than the best tin surface or the best passivated aluminum surface.

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STORABLE CONCENTRATED HYDROGEN PEROXIDE

Introduction

The design of systems employing concentrated hydrogen peroxide (HP) requires allowance in one form or another for the decomposition of a small fraction of the peroxide in the system tanks and lines. For systems intended for long term storage under sealed conditions this allowance must be in the form of ullage space and vessel wall strength in order to confine the gas liberated by decomposition of the peroxide. The present investigation has been concerned with means of reducing the amount of decomposition of concentrated HP which would occur under storage conditions as a result of 1) dissolved and suspended contaminants in the liquid phase, 2) catalytic activity of the container surfaces submerged in the HP and 3) catalytic activity of the container surfaces not submerged but in contact with the vapor from the HP. As in the previous reports from these laboratories on this subject the decomposition rates stemming from these sources will be separated whenever possible and will each be treated as first order reactions with respect to HP concentration. The assumption that the reaction is first order rather than a higher or a zero order will cause no significant errors in decomposition calculations as long as minor changes in HP concentration occur. In comparing surface activity measurements made with HP-90 and HP-98 differences may appear if the actual reaction mechanism is other than first order in HP concentration.

In the following data, therefore, the rate constants for the homogeneous liquid phase decomposition will be designated k_1, that for the heterogeneous reaction on submerged surfaces will be designated k_2 and that for the heterogeneous reaction on non-submerged surfaces will be designated k_3. In line with previous measurements an Arrhenius type activation energy will be assumed to apply to all three rate constants in extrapolating and comparing rates at various temperatures other than those specified for the particular measurement. In all cases the rates are determined by gas evolution methods instead of chemical analysis since the expected change in composition in most samples is too small for the latter method to give accurate results. The gas evolution method also allows for differential rate determination during the course of observations.

Objectives of the Program

The investigation of methods of purification and stabilization of HP and means of preparing and passivating inactive surfaces for contact with HP will be continued in order that storage of concentrated HP in sealed containers for periods up to 5 years might be feasible.

The scope of the investigation will be:

1. To continue laboratory investigation of ion-exchange, distillation and recrystallization techniques for purification of 90% to 98% HP in order to reduce the rate of homogeneous decomposition;

2. to continue laboratory investigation of tin plating on aluminum and on steel in order to achieve inactive tin surfaces;

3. to investigate additional materials of construction which have attractive physical or chemical properties for tentative use with concentrated HP;

4. to continue laboratory investigation of means of passivating surfaces of materials of construction for intended use with concentrated HP;

5. to develop ion-exchange equipment for processing quantities of HP;

6. to demonstrate with samples of HP of 5 gallon size, stabilized and stored at 25°C, the various purification techniques and surface coatings developed in the laboratory studies;

7. to continue the observation of the storage samples already in existence which are demonstrating stabilization formulas in HP-90, and which are stored in pyrex, aluminum and Kel-F lined aluminum containers.

Observation of Previously Stored Samples

Monitoring has continued of the samples in 5-gal containers which were placed in storage a year or more ago. Since the previous quarterly report only one sample has shown a significant change in trend - the sample with the initial concentration of 1 mg/1 as tin. The decomposition rate of this sample appears to have leveled off at about the same rate as three unstabilized samples after having increased steadily during the previous year. This would imply that the effective complex of tin and metallic ions had been reduced to near zero with the exception of the tin-aluminum complex.

According to Hood et al[a] and Lewis and Walters[b] the precipitation of the tin-aluminum complex begins when the molecular ratio of tin to aluminum is reduced to about 8 or less by increase in aluminum ion concentration. For the above example this would require only 0.03 mg/1 of aluminum. Although the original analysis of this feedstock showed less than 0.02 mg/1 of aluminum, the higher concentration would be easily attainable in HP-90 in an aluminum vessel.

The 3 unstabilized samples showed slight increases in decomposition rate about 6 months ago and apparently are remaining constant at that level now.

The 2 samples stored in tin plated vessels and the 2 samples which were treated by ion-exchange have been discontinued and analyzed. The results are shown in Table 1. Chemical analysis for HP content has agreed well with that calculated for the samples on the basis of the total gas evolved. Chemical analysis for tin showed the HP in the tin lined vessels had picked up 4 mg/1 more than the amount added as stabilizer, presumably by corrosion of the tin

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a) Hood, G. C., Evans, R. J. and Pierotti, G. J., Ind. Eng. Chem. 50, 1212 (1958).

b) Lewis, T. J., and Walters, T. M., J. Appl. Chem. 10, 396 (1960).

Table 1. ANALYSES OF STORAGE SAMPLES

Sample	Container Surface	HP Charged	HP, %w		pH, Direct Reading	Residue, mg/l		Component, $10^6 \times$ m/l				Decomposition			
												Homogeneous		Total 25°C[d] yr^{-1}	k_2 25°C[e] cm/yr
			Analysis[a]	Calc[b]		100°C	500°C	Al	Sn[f]	NO_3^-	$PO_4^{\equiv}$	100°C Day^{-1}	25°C[c] yr^{-1}		
1023-B Increase	Electrolytic Tin	Shell Chem	90.0 -0.3	90.1 -0.2	0.12	14.2 -3.5	11.2 +4.8	3.7 +2.5	67 +33	148	2.9 -1.0	0.0005	0.0004	0.0049	0.021
1024 Increase	Electrolytic Tin	Shell Chem	91.4 -0.8	91.4 -0.8	-0.90	25.5 +19.7	21.0 +20.0	5.6 +0.4	74 +40	128	2.3 -	0.0008	0.0007	0.116	0.054
1019-B Increase	Pyrex	Electrolytic[i]	87.4[h] -1.0	88.4 -0.3	0.65	27.3 -5.3	22.3 +5.9	7.4 +4.8	10 -39	173	<0.7 -	0.0032	0.0026	0.0035[g]	0.0041
1022 Increase	1260 Aluminum	Electrolytic[i]	88.7[h] -0.1	88.5 -0.3	0.67	14.5 -0.6	10.5 +4.8	2.6 +1.8	2 -34	268	1.9 +1.6	0.0021	0.0017	0.0056	0.020
1019	1260 Aluminum	Electrolytic[i]											0.0021[j]	0.0074	0.027

a) Chemical analysis by $KMnO_4$ method.

b) Calculated on the basis of the total gas evolved and collected during the storage period. Correction was made for water vapor and HP vapor in the gas phase and for the change in concentration resulting from the water retained by the HP.

c) Extrapolated using an Arrhenius activation energy of 18 kcal/mole.

d) Measurements made in the 5 gal container over the previous 3 months.

e) Calculated from the difference between the total and the homogeneous decompositions divided by S/V.

f) $Na_2Sn(OH)_6$ added to charge at 36×10^{-6} m/l. HP charged to sample 1019-B also had tin present from original supplier at 13×10^{-6} m/l.

g) Total rate of decomposition increase in past month from 0.0023 to 0.0058 yr^{-1}. This would give values for k_2 from 0.0000 to 0.014 cm/day.

h) Loss of about 1.4% occurred during the ion exchange.

i) Treated with stannic acid ion-exchanger.

j) Measurement made after transfer of the HP to a 5-gal pyrex container.

surface. In one case the increased tin and added stabilizer was apparent in the observed evaporation residue; in the other sample the evaporation residue was similar to the original indicating that some precipitation must have occurred to remove material from the sample.

Analyses for tin in the two ion-exchange treated samples showed a loss of over 80% of the amount added as stabilizer or present in the original feedstock and all of the amount picked up during the treatment. In both samples the evaporation residue was less than that in the untreated feedstock indicating that material equivalent in weight to more than that added as stabilizer had precipitated or had been removed during the ion-exchange treatment. The amount of aluminum (0.1 mg/1) which would have been required to form the insoluble aluminum-tin complex was not found missing from the original content but could easily have been picked up from the aluminum containers used for storage vessels.

Samples were taken from the above 4 storage vessels and decomposition measurements were made at 100°C. Correction was made for the contribution made by the sample test flask on the basis of pretest measurements with a standard feedstock HP. These values were then extrapolated to 25°C in order to compare them with the total decomposition measured in the 5 gal containers. The difference is presumed to be due to heterogeneous decomposition occurring on the surface and, after division by the surface to volume ratio of the container, gives the values for the surface activity, k_2, at 25°C. The values for k_2 for the tin-lined containers are 26 and 67 times as active as the lowest value obtained on tin which had been electroplated onto tin metal. The value similarly calculated for the pyrex container (sample 1019-B) is only approximate since wide variation in the total decomposition was measured prior to this sampling.

The value for k_2 calculated for the 1260 aluminum vessel (sample 1022) is also 14 times as high as the best value obtained for 1260 aluminum after contact with hot HP but in reasonable agreement with that for 1260 aluminum prior to this treatment. An additional measurement was obtained on this particular container in a previous test (sample 1019) in which the HP was observed and later transferred to the pyrex vessel as sample 1019-B. Assuming that essentially all of the decomposition was the homogeneous decomposition in sample 1019-B (as confirmed by the agreement between the calculated rate for 25°C as compared to the original measured rate in this vessel), then the surface activity calculated for sample 1019 is very nearly the same as that calculated for sample 1022. The difference may be real and indicates an improvement with time.

The homogeneous decomposition of the treated HP shown in samples 1019, 1019-B and 1022 indicates that improvement in the stability of the HP feedstock was accomplished by the treatment with β-stannic acid. The homogeneous decomposition rate of the feedstock, extrapolated from measurements made at 100°C, was 0.0064 yr^{-1} at 25°C. The second sample prepared by ion-exchange treatment of this feedstock showed a homogeneous decomposition of 0.0017 yr^{-1} at 25°C indicating an improvement by a factor of 4 over the unstabilized value but only a factor of about 3 over that achieved with the same level of stabilization of the original. This rate of homogeneous decomposition is not as low as can be achieved by other means of purification since the HP used in samples 1023-B and 1024 as well as that stored in pyrex (sample 1013-B), which was from a different method of production, has shown homogeneous decomposition rates of 0.0003 to 0.0007 yr^{-1} at 25°C. Additional samples of HP purified by the ion-exchange technique will be prepared for storage in the future.

Purification of HP

In order to reduce the decomposition occurring in the liquid phase the suspended and dissolved catalytic elements must be complexed in such a way that their catalytic efficiency is nullified or they must be removed from the solution. The chelating agents so far found effective for use with HP do not complex all of the common catalytic ions found in HP or at least do not completely eliminate their catalytic activity. Therefore methods for further purifying the HP and removing the suspended and dissolved material are being pursued.

Ion Exchange

Earlier success with the use of the insoluble alpha-and beta-stannic acid as inorganic ion-exchange media has been followed by examination of several other insoluble inorganic solids potentially effective for this purpose with HP. Several combinations of these agents have also been tried on the assumption that one may be a better anion exchanger and another a better cation exchanger thereby affording the best chance of removing both types of ions. In this way the catalytic chromate ion might be absorbed.

Tests of several different compounds and combinations completed in this quarter are shown in Table 2. The molecular sieve 5A previously used gave an effluent having a relatively high pH. This material was treated with 1% nitric acid in an attempt to reduced the pH of the effluent to a more usable range. Although, as shown in Table 2, the pH was reduced by the above treatment, it was still too high for practical use and the stability of the effluent was only slightly improved. A stronger acid treatment would probably break down the cellular structure of the molecular sieve.

A sample of β-stannic acid (batch No. 2) which had been used as an exchanger until it became partially ineffective was given a regeneration treatment with 70% nitric acid, washed well with ion-exchanged distilled water and reused with Becco HP-98 as feed. The effluent showed (sample No. 171) a decomposition rate as low as the pretest HP standard and approximately 1/3 that of the feedstock, after allowance of about 0.0004 day^{-1} is made for the effect of the test vessel walls. The acid solution used for this regeneration was analyzed in an attempt to disclose the type of impurities which had been absorbed from the HP. The results are discussed later.

Another bed of β-stannic acid (batch No. 5) was also treated with 70% nitric acid and then used to treat Becco HP-98 (sample No. 170). This also gave effluent with decomposition rate as low as the HP standard used in

Table 2. DECOMPOSITION RATES OF ION-EXCHANGE EFFLUENT AT 100°C

Ref No.[e] 9796-	Bed Size[a]		Effluent, Accumulative			Sample No.	pH[c]	Decomposition,[d] Day^{-1} at 100°C		
	cc	1/d	ml	Bed Vol	LHSV[b]			Pretest	Sample	Stabilized
With Molecular Sieve 5A, Unbonded, Acid Treated[f]										
13	8.5	1.7	350	41	19	131	1.58	0.0011	0.0063	0.0037
With β-Stannic Acid Solids, 2										
9[g]	8.2	6.0	3000	366	4.6	85	0.12	0.0011	0.0030	0.0026
(h)	"	"	3650	445	9.2	126	0.68	0.0009	0.0036	0.0022
(h)(i)	"	"	3900	476	8.7	149	-0.16	0.0010	0.0027	0.0015
24[i][j]	8.1	6.2	4200	513	15	171	-1.57	0.0010	0.0011	0.0011
With β-Stannic Acid Solids, 5										
23[i]	7.5	4.2	300	40	17	170	-1.43	0.0009	0.0008	0.0010
(g)	"	"	650	87	17	186	-0.20	0.0010	0.0020	0.0020
With Acidic Stannic Phosphate and β-Stannic Acid, 4, in Series										
19	7.7,5.4	3.1	400	74	24	127	-0.82	0.0010	0.0020	0.0017
(i)	" "	"	1250	232	2	176	-0.43	0.0008	0.0014	0.0015
With α-Stannic Acid, 3, and β-Stannic Acid, 4, in Series										
21[g]	5.2,7.2	2.3	600	83	14	134	1.88	0.0012	0.0021	0.0019
(g)	" "	"	700	97	10	133	2.03	0.0011	0.0023	0.0021
	" "	"	1000	139	9.8	138	2.01	0.0009	0.0045	-
	" "	"	1100	153	9.0	137	2.03	0.0010	0.0043	0.0015
(i)	" "	"	1550	215	13	139	1.09	0.0015	0.0023	0.0037
With α-Stannic Acid, 3, and β-Stannic Acid, 4, Mixed										
25[i]	12	8.8	350	29	7.8	187	0.15	0.0019	0.0025	0.0025

a) Bed size measured wet with HP-90 and, therefore, expanded. 1/d is the ratio of the length to the average diameter and is approximate since the diameter expands near the inlet filter. Where two beds are used in series, the 1/d refers to the final bed only.

b) Liquid hourly space velocity in terms of bed volumes per hour.

c) Direct reading with glass-Calomel cells. When effluent was basic, greater than 0.8 for HP-90, the sample was neutralized with HNO_3 before measuring the decomposition rate.

d) Values are uncorrected for the contribution by the vessel walls. The pretests were with a standard stabilized HP-90 and indicate that approximately 0.0006 day^{-1} is due to this HP and the remaining to the vessel. For the test sample the difference above the pretest plus about 0.0006 day^{-1} is due to the sample HP.

e) Electrolytic HP-90 was used for feed except where noted otherwise. Decomposition of untreated feed approximately 0.0094 day^{-1} at 100°C.

f) Treated with 1% HNO_3 in order to reduce the pH of the effluent.

g) Du Pont nonelectrolytic HP-90 used as feed. Decomposition of untreated feed approximately 0.0034 day^{-1} at 100°C.

h) HP in downward flow through bed.

i) Becco HP-98 used as feed. Decomposition of untreated feed approximately 0.0025 day^{-1} at 100°C.

j) Stannic acid solids were regenerated with 70% HNO_3.

the pretest. Further stabilisation of this effluent, as well as sample No. 171 above, was not effective in reducing the decomposition rate below this level. This bed was next used to treat du Pont nonelectrolytic HP-90 (sample No. 186) but only reduced the decomposition rate by a factor of 2, after allowance of about 0.0004 day^{-1} is made for the effect of the test vessel walls.

Since previous tests with stannic phosphate alone or in series with used beds of stannic acid had been without success a further test was made using a fresh bed of β-stannic acid as the final treatment following passage of the HP through a bed of acidic stannic phosphate. Both the electrolytic HP-90 and the HP-98 feedstocks were improved significantly in stability (samples 127 and 176) over their untreated values but apparently not as much as by the stannic acid alone.

Fresh beds of α-stannic acid and β-stannic acid were also used in series for treating the three HP feedstocks as shown in samples 133, 134, 137, 138 and 139. The stability of none of these samples was improved to the level of the pretest samples or the samples treated with β-stannic acid alone.

The beds used alone were then mixed together into one larger bed and used to treat the HP-98 feedstock (sample 187). The results were comparable with those of the beds in series except that the apparent pH of the effluent was less basic.

The above results indicate that the β-stannic acid alone is a better exchange media than any combination yet tried. This would imply that some contaminants were being picked up from the other beds when used in combination with the stannic acid or that a shorter length of contact time is optimum before solution of the media into the HP takes place and thereby introduces contaminants back into the solution. Analyses of effluent and of exchange media in order to ascertain which ions are absorbed have only been partially successful.

Where the phosphate bed was used analyses show that sufficient hydrolysis occurs to place more than 40×10^{-6} moles/liter of phosphorus into solution without a corresponding amount of tin, as shown in Table 3. It is assumed that the tin remained in the exchange bed as hydrated oxide although the high evaporation residue of one sample suggests that some suspended insoluble exchange media may also have come through the final filter with the effluent HP. Use of β-stannic acid exchanger after the phosphate bed reduces the phosphorus content significantly but in these tests an appreciable amount still was retained in the effluent.

Stannic acid beds passed variable amounts of tin through into the final effluent, partly as suspended solid. Since this amount would depend on the efficiency of the final filter the most pertinent data are the amounts of soluble tin in the effluent. Three samples indicate that soluble tin stabilizer is not absorbed by the stannic acid - one sample indicates that part of it was. The degree of coagulation of the colloidal hydrated stabiliser would probably be the controlling factor allowing the tin to be filtered out but not absorbed on the exchange medium.

Table 3. COMPOSITION OF HP EFFLUENT

Ion Exchange Bed	Effluent Composition,[a] 10^6 x m/l					Evaporation Residue, mg/l	
	Sn	P	Al	SO_4	NO_3	100°C	500°C
With Electrolytic HP-90, B-1155							
None, feedstock	<1.7	<0.3	<1.0	6.3	89	15.1	5.7
β-Stannic acid	3.4	<0.6					
α- and β-stannic acids, series	21						
Stannic phosphate, basic	1.0	42	7.0	16.0	87	150.0	140.0
Stannic phosphate, acidic	1.0	61					
Stannic phosphate, acidic and basic, series		480	2.2	34	33	32	32
Stannic phosphate, β-stannic acid, series		19					
With Nonelectrolytic du Pont HP-90, D275							
None, feedstock	28	1.6	6.7	15		39	25
α-Stannic acid	39	0.4	1.6	19		17.8	8.0
β-Stannic acid	28	<0.3	3.3	17		20.7	10.4
α- and β-Stannic acids, series	45						
With Becco HP-98, B-1198							
None, feedstock	8.4	0.6	5.9	13		26	16
β-Stannic acid	1.4						
α- and β-Stannic acids, mixed	100						
Stannic phosphate, β-stannic acid, series	8.4	4.2	1.1	40	69	10	3.8

a) Complete analyses on every sample was not considered to be justifiable.

The stannic acid beds appear to remove part of the phosphorus and aluminum and reduce the evaporation residue content of the feedstock HP. On this basis it is assumed that other metallic ions would also be absorbed thereby giving the improved stability observed in the effluent. Absorption of the nitrate and sulfate anions appears to be nil. Therefore, it is assumed that chromate ion would not be removed by this medium.

Analyses of the stannic acid solids by spectrometric methods and chemical analyses of strong acid elutions have failed to show significant amounts of iron, chromium or copper as absorbed elements. The total amounts found in the strong acid eluent of a used bed of stannic acid was the same as found in the acid used and in the eluent of fresh stannic acid. Dilute ammonia elutions of used beds gave similar results. The concentrations of elements found, uncorrected for that contributed by the acid or base used, when calculated on the basis of the total HP contacted with the beds would indicate concentrations in the HP of the order 10^{-8} m/1 or less. This level is well below the limit of detection in the HP by direct analysis.

Distillation

A distillation unit is being constructed for preparing distilled HP of 90-98% concentration according to the procedure discussed in the previous quarterly report under this contract.[a] Details of the unit will be described after it has been completed and placed in operation.

Studies of Container Surfaces

Surface Activities

Three additional aluminum alloys have been tested with stabilized HP-90 for catalytic activity toward decomposing the HP and results are shown in Table 4. Also shown in the table are the results of tests on 3 alloys with HP-98 (as received with 1 mg/1 tin as stabilizer) compared to previous tests and additional tests on these same samples with HP-90. Also shown are the results of further tests on Kel-F plastic and the fluoro-ethylene-propylene (FEP) Teflon. The procedures for surface preparation of these samples are given in Table 5.

The activities of the 2014 and 2219 aluminum, after caustic and nitric acid treatments, are considerably greater than shown by the aluminum alloys previously tested in this program. This is expected because of the high copper content of the alloy. Also as expected is the contamination of the HP as a result of contact with these alloys, as shown by the blank obtained after contact. However, the activity of the 2014 alloy after contact with hot HP even a 9 hour period is surprisingly low. Apparently the corrosive action of the HP has removed the copper atoms from the surface and left a relatively pure aluminum oxide film exposed. After this hot HP treatment the overall decomposition rate is similar to alloy 6053. Alloy 2219 did not respond in the same manner on contact with hot HP. Although the activity decreased, the rate of contamination of fresh HP in contact with it was relatively fast even

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[a] Monger, J. M., AFRPL-TR-66-207, March-May 1966.

Table 4. SURFACE ACTIVITIES IN STABILIZED HP AT 100°C

Sample No.	HP No.[c)]	Surface		S/V, cm^{-1}	Decomposition Rate		
		Type	Preparation[a)]		Overall, Day^{-1}	Blank,[b)] Day^{-1}	k_s, cm/day
181	A18-2	2014 Aluminum[d)]	1,2,5,6	1.01	0.150	0.0066	0.141
"	"	" "	1,2,5,6,7	0.95	0.0156	0.0139[e)]	0.0018
184	A18-2	2219 Aluminum[d)]	1,2,5,6	0.95	1.8	0.008	1.9
"	"	" "	1,2,5,6,7	1.02	0.196	0.142[e)]	0.053
116	A18-2	7039 Aluminum	1	2.29	0.343	0.0010	0.149
"	"	" "	1,7	2.97	0.0856	0.0127	0.024
132	"	" "	1,2,5,6	2.49	0.0709	0.0003	0.028
"	"	" "	1,2,5,6,7	4.53	0.0723	0.0090	0.0140
168	"	" " d)	1,2,5,6	1.07	0.0562	0.0063	0.047
"	"	" " d)	1,2,5,6,7	1.05	0.0204	0.0063	0.0134
174	"	" "	1,2,5,6,7	2.32	0.0364	0.0013	0.0151
"	B1198	" "	1,2,5,6,7	4.30	0.0682	0.0314	0.0086
"	A18-2	" "	1,2,5,6,7	4.24	0.0589	0.0063	0.0124
"	B1198	" "	1,2,5,6,7	4.39	0.0960	0.0050	0.0207
"	"	" "	1,2,5,6,7	4.67	0.124	0.006	0.0252
36	A18-2	1260 Aluminum	1,2,5,6,7	2.07	0.0066	0.0032	0.0016
119	B1198	" "	1,2,5,6,7	1.97	0.0108	0.0024	0.0043
"	"	" "	1,2,5,6,7	2.22	0.0098	0.0025	0.0033
25	A18-2	5052 Aluminum	1,2,5,6,7	2.93	0.0124	0.0065	0.0020
120	B1198	" "	1,2,5,6,7	2.22	0.0168	0.0024	0.0065
"	"	" "	1,2,5,6,7	2.97	0.0145	0.0047	0.0033
92	A18-2	Kel-F	6	3.75	0.0191	0.0011	0.0048
"	"	"	6.7	4.68	0.0202	0.0015	0.0040
99	A18-2	Teflon FEP	6	6.02	0.0717	0.0027	0.0115
"	"	" "	6,7	6.97	0.0733	0.0011	0.0111

a) Surface preparation according to Table 5.

b) For samples without treatment 7 the blank is determined before addition of the test sample. With treatment 7, after repeated replacement of HP, the blank is determined after test and removal of the sample. The blank includes the homogeneous decomposition by contaminants and the heterogeneous decomposition due to the vessel walls, including any contaminants absorbed there.

c) HP-90 from drum A18 with $Na_2Sn(OH)_6$ at 34 x 10^{-6} m/1 and HNO_3 at 69 x 10^{-6} m/1 added as stabilizer, or HP-98 from drum B1198 which has tin at 8.4 x 10^{-6} m/1 present as stabilizer.

d) Test sample is a 3-in. diameter disc fitted to a special test vessel. Initial blank is obtained by substituting a pyrex disc.

e) Final blank obtained by transferring the HP to a standard test flask.

Table 5. DESCRIPTION OF TREATMENTS EMPLOYED IN PREPARATION OF SURFACES

Treatment Number	Procedure[a)]
1	Sample degreased in aromatic solvent followed by a rinse in acetone, all at room temperature.
2	Sample submerged in 1% NaOH for 10 minutes at room temp.
3	Sample submerged in 10% NaOH for 16 hours at room temp.
4	Sample submerged in 1% HNO_3 for 5 minutes at room temp.
5	Sample submerged in 35% HNO_3 for 16 hours at room temp.
6	Sample submerged in HP-90 until used for test, at room temperature.
7	Sample submerged in stabilized HP-90 at the temperature of the test for 1 to 16 hour periods, followed by repeat treatments with fresh HP-90 until steady state conditions appear to be achieved.
8	Sample submerged in fused stearic acid for 1 hour at 80-100°C immediately after treatment by No. 2 procedure.
9	Sample submerged in 2% ethylene-diaminetetraacetic acid in 30% H_2SO_4 for 30 minutes at 80-90°C.
10	Sample submerged in 1% disodium ethylenediaminetetraacetic acid in 35% HNO_3.
11	Sample submerged in fused phthalic anhydride for 1 hour at 140-150°C immediately after treatment by No. 2 procedure.
12	Sample submerged in Viscasil 100,000, then wiped dry with absorbent tissue.
14	Sample submerged in 85% H_3PO_4 for 16 hours at room temp.
15	Sample submerged in 35% HNO_3 for 1 hour at 50-70°C.
16	Sample submerged in 1% Viscasil in benzene, dried, resubmerged and dried.
18	Sample anodized in 25% H_3PO_4 at 1 amp/sq decimeter for 6 minutes at room temperature.

a) Each procedure is followed by thorough rinsing in deionized distilled water before further treatment.

after 9 hours contact with hot HP. The level of contamination by this alloy is 10 times greater than that of any other aluminum alloy tested.

Alloy 7039 without pretreatment behaves in a manner similar to some of the more pure alloys previously tested. The caustic and nitric acid pretreatment does not achieve the improvement exhibited by these other alloys, however. The lowest surface activity achieved is high, second only to alloy 2219 among those tested in this program. The rate of contamination of the HP is well below that of the 2219 alloy.

Surface activity measurements using 98% HP were conflicting in their results on the aluminum alloys. On the 7039 aluminum the values appeared to increase with time as if adsorption of active species onto the surface were occurring. One activity measurement was below that obtained with HP-90 but all others were 40 to 200% higher. Some fluctuation might be expected due to the low stabilizer concentration, however, these data do not show conclusively whether the activity in 98% is greater or equal to the activity in 90%. More data were obtained with steel surfaces and these results are discussed later.

The passivation effect of hot HP on the aluminum surfaces is shown in Figures 1 and 2. In Figure 1 the aluminum alloys 1260, 5052 and 6061 are shown as tested with only solvent degreasing as the pretreatment of the surface. The values shown are the total decomposition rates measured over the period of time that the sample was in contact with fresh HP, with each symbol representing a new charge of fresh HP. More rapid passivation would probably have occurred with more frequent replacement of the HP.

Figure 2 shows the similarly obtained values after the aluminum surfaces were cleaned with the standard caustic and nitric acid treatment. The initial decomposition rates in this case are less by factors of 10 to 40. For the 5052 sample the intermediate values were not obtained because of experimental difficulties but are presumed to have decreased in a manner similar to the 6061 alloy. The other alloys tested in this program behaved in a similar manner with the initial and final values being as shown in previous tables.

These curves imply that the chemical action of the HP preferentially dissolves the more active elements until a steady state condition is achieved in which the aluminum oxide prevents further corrosion except at the rate of dissolution of the aluminum oxide.

Additional measurements were made on Kel-F plastic using a larger surface/volume ratio in order to obtain a value less influenced by the blank. The values given in Table 4 show little change on long contact with hot HP and were consistent over a 57 hour test. Although the surface activity is higher than the best obtained with aluminum there is essentially no contamination of the HP.

Fluoroethylene-propylene (FEP) Teflon, which has quite different properties than TEF Teflon, was also tested over a 28 hour period with essentially no change in surface activity. The surface activity was significantly higher than that of TEF Teflon. No contamination of the HP was apparent.

Figures 1 and 2 follow

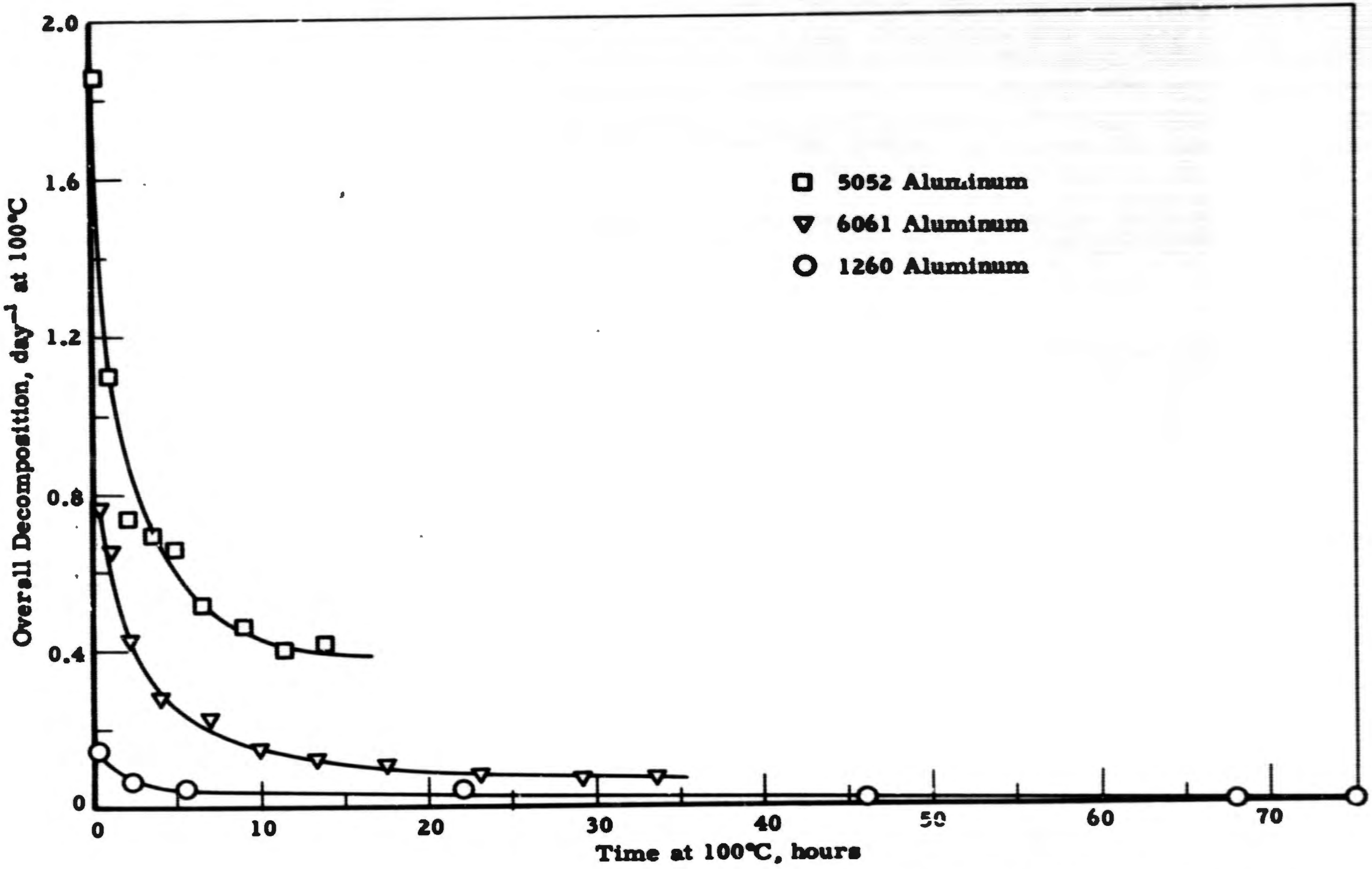

Figure 1. PASSIVATION ACTION OF HOT HP ON DEGREASED ALUMINUM

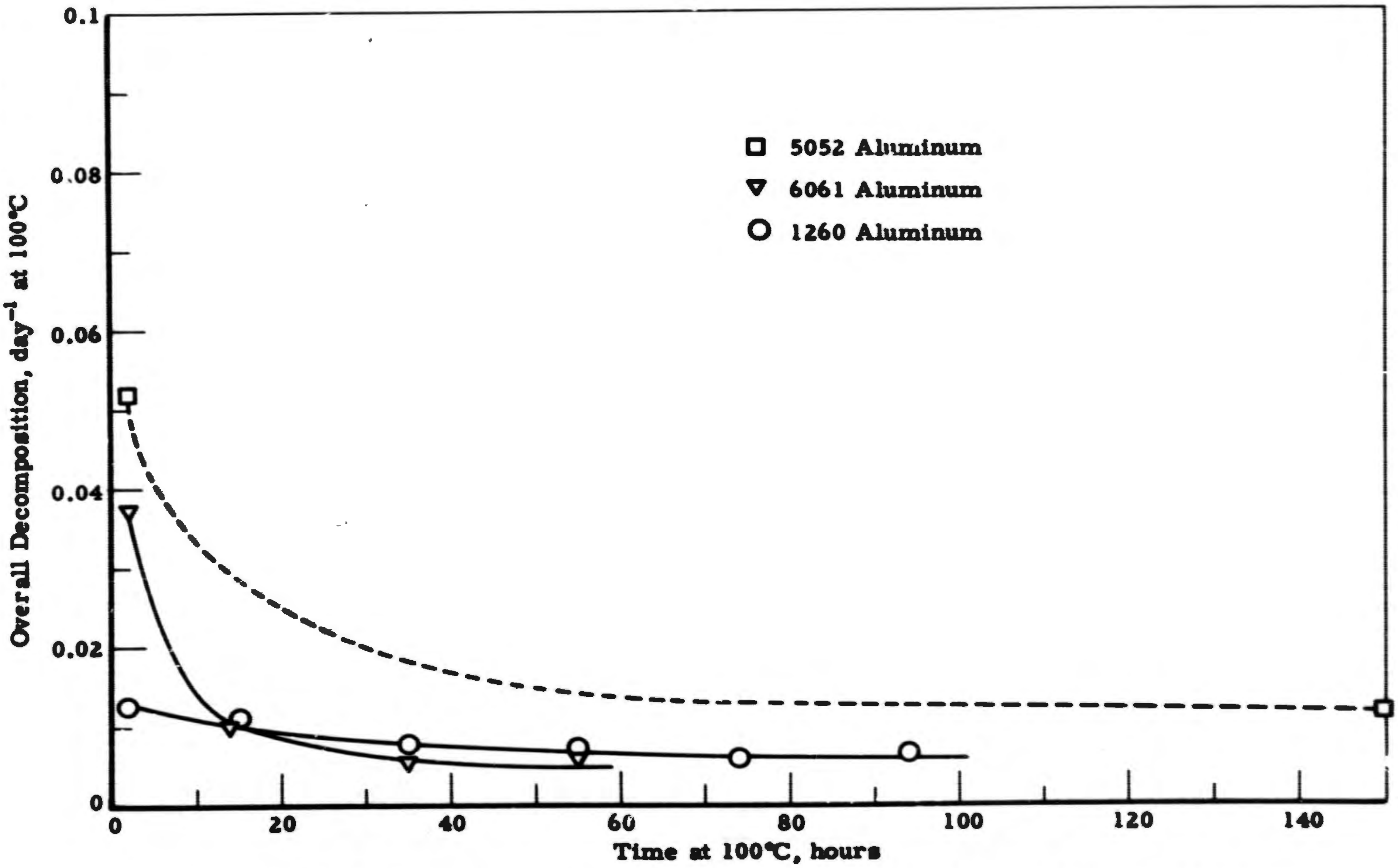

Figure 2. PASSIVATION ACTION OF HOT HP ON CHEMICALLY TREATED ALUMINUM

Several other surface treating procedures were tried on 1260 aluminum and on 301-T stainless steel in an effort to reduce the surface activities below those previously measured. The results are shown in Table 6. The various treatments used are given in Table 5. The stearic acid treatment was tried as a potential coating material which may have formed a chemical bond with the aluminum. The ethylenediaminetetraacetic acid in sulfuric and in nitric acid solution and the phthalic anhydride were tried as chelating agents which may have removed some of the active metallic elements from the surfaces. The Viscasil 100,000[a)] treatments were used in order to test out a procedure used satisfactorily on more dilute HP solutions elsewhere.[b)] Phosphoric acid treatment is commonly used as a pickling agent for stainless steel and also is a chelating agent.

With 1260 aluminum, the initial activities measured were all lower than that obtained with 1260 aluminum which had only been degreased with solvent, and the initial activities measured after treatment with hot phthalic anhydride or with EDTA in sulfuric or nitric acid were comparable to those obtained after treatment with 35% HNO_3. However, after contact with hot HP, only the sample treated with EDTA in HNO_3 showed activity as low as that obtained after solvent degreasing or HNO_3 treatment followed by contact with hot HP. The sample treated with phthalic anhydride was only slightly more active. The sample anodized in H_3PO_4 was less than half as active as one previously anodized in 15% H_2SO_4 but more active than one anodized in sodium stannate and nearly 7 times as active as the nonanodized aluminum.

Stainless steel type 301-T was slightly more active after the EDTA in HNO_3 treatment than either the solvent degreased or nitric acid treated metal. This difference was largely removed on contact with the hot HP. The difference may have been experimental error or may have resulted from a small chemical change in the surface. Phosphoric acid pickling gave an initial activity similar to that measured on the nitric acid treated sample but with further contact with hot HP the activity increased. The chemical nature of this surface was different than that of the former as shown by its failure to become bronzed in color by the 3 hour contact with hot HP. Treatment with the highly viscous water-repellant Viscasil 100,000 succeeded in one sample in reducing the surface activity by about 30% but was not a permanent coating as was shown by the significant area which became bronzed in color from contact with hot HP. Application of thicker films of this material might increase the time required for the HP to reach the metallic surface but would also increase the explosion hazard since this material in contact with HP-90 is impact sensitive.

Additional measurements of surface activity have been obtained on stainless steel alloys after surface preparation by the degreasing, caustic and nitric acid procedures. The activities in contact with HP-90 and HP-98 are shown in Table 7.

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a) Viscasil 100,000 is a dimethyl silicone fluid made by General Electric and having a viscosity of 100,000 centistokes at 25°C.

b) Haskell, W. W., Wood River Research Laboratory, Shell Oil Company, private communication.

Table 6. EFFECT OF SURFACE TREATMENT ON THE SURFACE ACTIVITY AT 100°C

Sample No.	HP No.[c)]	Surface		S/V, cm^{-1}	Decomposition Rate		
		Type	Preparation[a)]		Overall, Day^{-1}	Blank,[b)] Day^{-1}	k_s, cm/day
61	A18-2	1260 Aluminum	1,2,8	1.90	0.0626	0.0009	0.032
"	"	" "	1,2,8,7	2.29	0.0309	0.0144	0.0072
110	A18-2	1260 Aluminum	1,2,9	1.71	0.0168	0.0008	0.0094
"	"	" "	1,2,9,7	2.18	0.0164	0.0042	0.0056
111	A18-2	1260 Aluminum	1,2,10	2.06	0.0148	0.0009	0.0067
"	"	" "	1,2,10,7	2.66	0.0093	0.0048	0.0017
101	A18-2	1260 Aluminum	1,2,11	1.65	0.0135	0.0009	0.0077
"	"	" "	1,2,11,7	2.19	0.0098	0.0053	0.0021
163	A18-2	1260 Aluminum	18	2.01	0.0459	0.0051	0.020
"	"	" "	18,7	2.08	0.0325	0.0111	0.0103
144	A18-2	301-T S. Steel	1,3,10	1.85	3.84	0.0019	2.07
136	A18-2	301-T S. Steel	1,12	2.15	3.03	0.0011	1.41
143	A18-2	301-T S. Steel	1,3,14	2.25	5.47	0.0009	2.42
Surface Acitivity at 80°C							
144	A18-2	301-T S. Steel	1,3,10	1.85	1.68	0.000	0.91
"	"	" " "	1,3,10,7[d)]	2.24	1.63	0.029	0.72
136	A18-2	301-T S. Steel	1,12,7[d)]	2.76	1.21	0.083	0.41
143	A18-2	301-T S. Steel	1,3,14	2.25	1.49	0.000	0.66
"	"	" " "	1,3,14,7	2.76	3.11	0.243	1.04
159	A18-2	301-T S. Steel	15,16[d)]	2.15	1.16	0.001	0.54

a) Surface preparation according to Table 5.

b) For samples without treatment 7 the blank is determined before addition of the test sample. With treatment 7, after repeated replacement of HP, the blank is determined after test and removal of the sample. The blank includes the homogeneous decomposition by contaminants and the heterogeneous decomposition due to the vessel walls, including any contaminants absorbed there.

c) HP-90 from drum A18 with $Na_2Sn(OH)_6$ at 34 x 10^{-6} m/l and HNO_3 at 69 x 10^{-6} m/l added as stabilizer, or HP-98 from drum B1198 which has tin at 8.4 x 10^{-6} m/l present as stabilizer.

d) Sample surface became bronzed by the hot HP.

Table 7. SURFACE ACTIVITIES IN STABILIZED HP AT 80°C

Sample No.	HP No.[c)]	Surface		S/V, cm^{-1}	Decomposition Rate		
		Type	Preparation[a)]		Overall, Day^{-1}	Blank,[b)] Day^{-1}	k_2, cm/day
121	B1198	301-T S. Steel	1,7[d)]	1.68	1.37	0.000	0.82
"	"	" " "	1,7	2.10	1.31	0.004	0.62
130	A18-2	301-T S. Steel	1,3,5,6,7[d)]	1.83	1.12	0.001	0.61
"	"	" " "	1,3,5,6,7[e)]	1.83	1.29	0.659	0.34
129	A18-2	347 S. Steel	1,3,5,6,7[d)]	1.72	0.944	0.001	0.55
"	"	" " "	1,3,5,6,7[e)]	1.72	1.38	0.544	0.48
118	A18-2	AM355 S. Steel	1,3,5,6	1.74	1.13	0.000	0.64
"	"	" " "	1,3,5,6,7[f)]	2.39	2.15	0.146	0.84
117	A18-2	Almar 18-250	1,3,5,6	1.85	0.074	0.001	0.039
"	"	" "	1,3,5,6,7	2.15	0.095	0.006	0.041
175	A18-2	" "	1,3,5,6,7	1.95	0.187	0.006	0.093
"	B1198	" "	1,3,5,6,7	2.11	0.109	0.004	0.083
"	A18-2	" "	1,3,5,6,7	2.14	0.086	0.005	0.038
"	B1193	" "	1,3,5,6,7	2.05	0.112	0.002	0.054
Surface Activity at 25°C[e)]							
129	A18-2	347 S. Steel	1,3,5,6,7	1.72	0.00588	0.00182	0.00236
Surface Activity at 0°C[e)]							
130	A18-2	301-T S. Steel	1,3,5,6,7	1.83	0.00035	0.00010	0.00014

a) Surface preparation according to Table 5.

b) For samples without treatment 7 the blank is determined before addition of the test sample. With treatment 7, after repeated replacement of HP, the blank is determined after test and removal of the sample. The blank includes the homogeneous decomposition by contaminants and the heterogeneous decomposition due to the vessel walls, including any contaminants absorbed there.

c) HP-90 from drum A18 with $Na_2Sn(OH)_6$ at 34 x 10^{-6} m/l and HNO_3 at 69 x 10^{-6} m/l added as stabilizer, or HP-98 from drum B1198 which has tin at 8.4 x 10^{-6} m/l present as stabilizer.

d) Sample surface became bronzed by the hot HP.

e) Measurements on these samples made at 25 or 0°C after the first measurement and before the second measurement at 80°C.

f) Sample surface became purplish blue in the hot HP.

The value for surface activity obtained on 301-T S.S. with HP-98 is essentially the same as that obtained on the same sample with HP-90. Contamination of the HP in the half-hour contact was relatively small. The contamination resulting from other 301 S.S. samples has been significantly higher.

Alloy AM355 stainless steel gave activity values of the same order as the 301 alloy after caustic and acid treatment and appeared to increase in activity on contact with hot HP. Contamination of the HP resulting from a half hour contact at 80°C was less than that from 304 alloy.

Almar 18-250 alloy showed activity an order of magnitude less than those above and about half that shown by this material with only solvent degreasing. With or without the acid treatment the activity after contact with hot HP is similar and is nearly the same as that of the Almar 18-200 alloy. The activity of the 18-250 alloy was tested again after standing in air for 1 month and showed an activity approximately equal to that of the solvent degreased sample.

Using HP-98 and HP-90 alternately on the above 18-250 sample again brought the activity down to the 0.04 cm/day level after about 16 hours contact. The apparent change in activity with time confuses the problem of assessing any change in activity with HP concentration, however, the final values indicate approximately 40% greater apparent activity in HP-98 than in HP-90. If the assumed 1st order reaction mechanism were in reality a zero order, reaction, a difference of 10% in the other direction would be expected. The observed difference in activities might be due to experimental error or the effect of the stabilizer concentration. Very little relative contamination of the HP occurred in any of the tests with the Almar 18-250 alloy.

One sample of 301 S.S. and one of 347 S.S. were measured in HP-90 at 80°C and immediately after at 0°C or 25°C, respectively and then again at 80°C. The final blank reading in each case was also measured at 80°C and at the lower temperature used for the sample. In both cases the final activity measurement at 80°C was slightly lower than the first. From this final value and the value measured at the lower temperature an Arrhenius type activation energy was calculated and found to be:

301 S.S.   0°C to 80°C   E = 18.6 kcal
347 S.S.   25°C to 80°C   E = 20.2 kcal

These values are in fair agreement with the 18 kcal value previously measured in these laboratories.

Electroplating

Additional experiments have been performed in electroplating tin onto aluminum surfaces. Variations in the pretreatment were performed in an attempt to prepare a firmly adhering tin film in a more reproducible manner. The steps which were varied included the formation of a zinc plate on the aluminum by dipping in sodium zincate-caustic solution or by electroplating zinc from a zinc cyanide solution, neutralizing the caustic adhering to the sample by dipping into dilute acid before tin plating, tin electroplating by the so-called "hot dip", fusing of the tin plate and tin plating in sulfuric or sulfamic acid baths. A number of additives to the tin plating baths have been suggested by various experimenters[a][b][c] and several of these were also tried. Other plating procedures, namely, plating a tin-zinc mixture[d] and plating onto an anodized surface,[e] were also tried but without the use of a primary copper electroplate in the latter case.

The basic approach to the problem of applying a tin plate over aluminum has been to apply first a zinc film by displacement of aluminum with zinc through electrochemical action followed by application of a tin plate by electroplating from sulfuric or sulfamic acid bath. The preliminary chemical treatment and the intermediate washes are also important in achieving the bonding between metals necessary to prevent peeling of the film.

Pretreatment with caustic, in order to remove the thick oxide film on the aluminum, and with dilute nitric acid, in order to fix a thin oxide coat, was a standard procedure. Long reaction time in caustic tended to increase the surface roughness, which affects bonding, but does not change the nature of surface bonding otherwise.

A thin, firmly attached film of zinc was applied by submerging in a sodium zincate-caustic bath for 30 seconds and was usually found to be improved by treating with dilute nitric acid and then rezincating. Whether the zinc adheres by a metal to metal bond at this point is questionable but may instead be bonded by a coordinated oxygen link similar to the sulfate metal network believed to be present in anodized films.[f] By the latter model the film would be noncontinuous, could be improved by alternate dissolution of some of the zinc and rezincating, and would leave a porous aluminum oxide underneath containing some electrolyte and capable of reacting chemically to form blisters under the succeeding metal plate. The double zincating treatments appeared to promote better tin adhesion than single zincating followed by zinc electroplating in a zinc chloride-sodium cyanide bath or than zincating followed by electroplating in a zinc cyanide-sodium stannate bath. The thinner films appeared to behave better than thicker ones. Failure of the tin plate usually occurred at the tin-zinc interface and was evident from blisters or from relative ease of peeling.

Since the application of the zinc or zinc-tin alloy film was accomplished in a basic solution whereas the tin plating was accomplished in

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a) "Modern Electroplating", F. A. Lowenheim, editor, Electrochemical Society, 1963.
b) Ollard, E. A. and Smith, E. B., "Handbook of Industrial Electroplating", 1964.
c) "Metal Finishing Guidebook", Metals and Plastics Publications, 1959.
d) Davis, P. E., Ordnance, September-October 1964, page 195.
e) "Suggested Method for Plating Copper on Aluminum", Technology Utilization Report, NASA-SP-5025, April 1966.
f) Murphy, J. F., "A Theory for the Formation of Anodic Oxide Coatings on Aluminum", Aluminum Development Association's Conference on Anodizing Aluminum, September 12-14, 1961, University of Nottingham, England.

an acid bath, the samples were given thorough rinsing and various degrees of neutralization in acid baths between these steps. Solutions of sulfuric, phosphoric, nitric and acetic acids were used in dilute concentrations in order that the zinc film would not be dissolved. Of these the most success appeared to follow use of 1 to 2% nitric acid for 1/2 to 1 minute. Without acid washing, blisters formed during the tin plating as if some of the caustic from the preceding bath were absorbed in the aluminum oxide and still reacting with the aluminum.

In the tin plating step the recommended "hot dip", i.e., having the voltage applied before the sample is introduced into the bath, was used at all times to prevent acid corrosion of the zinc film. Current densities of 0.02 amp/cm^2 were used. Stannous sulfate in sulfuric acid bath gave good deposits and in sulfamic acid bath gave better and more even deposits. This better throwing power of the sulfamic acid bath was enhanced by the use of gelatin, m-cresol, dihydroxydiphenyl sulfone, starch and dextrine as suggested by the various previous investigators quoted above. On nearly all samples which were tin plated the tin film was a strong continuous film. One exception was the tin deposited on aluminum which had been anodized in phosphoric acid.

Samples which did not form blisters during the plating procedure or which did not yield to small shear force applied by the end of a spatula were soaked in HP-90 for overnight and then tested at 100°C in HP-90. The results of these tests are given in Table 8. The procedures used in forming these test samples are given in Table 9.

Sample No. 112, tin deposited on type 5052 aluminum, gave initial and final surface activities very similar to that obtained for tin on 1260 aluminum, as reported previously. Since these activities were higher than those obtained before on tin electroplated from a sulfuric acid both the above samples were replated in a sulfuric acid bath and remeasured. Sample 145 shows an initial activity somewhat lower than sample 112 but the final activity is essentially the same. The sample was greenish-grey in color after 75 hours contact with hot HP. It is assumed that some of the constituents of the sulfamic bath may be carried in the tin film and into the test HP in some manner in order to give the higher initial result and the chemical change in the tin plate.

Samples 158 and 160, besides being zinc electroplated prior to the tin plating, were heated after being tin plated in order to melt the tin film. These samples were then given a second tin electroplate, which was brighter and more crystalline in appearance than the first tin coating. Both samples retained their metallic appearance during the hot HP test but No. 158 developed blisters over a large portion of the surface. Sample No. 160 developed a few small blisters and showed a surface activity of the same magnitude as the previous samples. Analysis of the HP after 18 hours contact at 100°C showed less than 0.01 mg/l of tin. Since no stannate stabilizer was added appearance of tin in this sample would have indicated corrosion of the plating.

Table 8. SURFACE ACTIVITY OF TIN PLATED SAMPLES AT 100°C

Sample No.	HP No.[c)]	Surface		S/V, cm^{-1}	Decomposition Rate		
		Type	Preparation[a)]		Overall, Day^{-1}	Blank,[b)] Day^{-1}	k_s, cm/day
112	A18-2	Tin on 5052 Aluminum	21	2.00	0.0536	0.0009	0.026
"	"	" " " "	21,7	3.05	0.0397	0.0126	0.0089
145	A18-3	Tin on 5052 Aluminum	21,22	1.77	0.0154	0.0068	0.0049
"	"	" " " "	21,22,7	2.33	0.0210	0.0015	0.0084
158	A18-3	Tin on 1260 Aluminum	25	2.61	0.0541	0.0041	0.0191
"	"	" " " "	25,7	2.62	0.0712	0.0395	0.0121
160	A18-3	Tin on 1260 Aluminum	25	2.15	0.0315	0.0047	0.0124
"	"	" " " "	25,7	2.22	0.0397	0.0261	0.0051

a) Surface preparation according to Table 9.
b) Blank determination performed in the same manner as in Table 4.
c) HP-90 from drum A18. A18-2 is with $Na_2Sn(OH)_6$ at 34 x 10^{-6} m/1 and HNO_3 at 69 x 10^{-6} m/1 added as stabilizer. A18-3 is without added stabilizer.

Table 9. TIN PLATING PROCEDURES

Treatment Number	Procedure
21	Samples submerged in 2% NaOH for 2 hours, then in 2% HNO_3 for 10 minutes, then zincated. Samples zincated in 16% Na_2ZnO_2 - 40% NaOH solution for 30 seconds at room temperature. Samples were then rinsed well and submerged in 2% HNO_3 for 1 minute. Samples were then zincated again, rinsed and submerged in 2 HNO_3 for 1 minute again. Samples were then electroplated by submerging in 6.4% stannous sulfate - 5.0% sulfamic acid - 0.5% dihydroxydiphenyl sulfone solution with the current on and maintained for 6 minutes at room temperature at 0.022 amp/cm^2 (20 amp/sq ft). Samples were then rinsed well and submerged in HP-90 for 20 hours.
22	Samples previously plated by procedure 21 were given an additional tin plate by submerging in 5.0% stannous sulfate - 5.0% sulfuric acid - 5.0% sodium sulfate - 0.4% gelatin - 0.2% m-cresol solution with the current on and maintained for 6 minutes at room temperature at 0.022 amp/cm^2. Samples were then rinsed well and submerged in HP-90 for 20 hours.
25	Samples were treated as in procedure 21 through the 1st zincating step. Samples were then zinc electroplated in 0.05% zinc chloride - 0.05% sodium cyanide - 1% sodium hydroxide solution for 1 minute at room temperature at 0.022 amp/cm^2. Samples were then rinsed and submerged in 2% HNO_3 for 1 minute and then tin electroplated as in 21. The tin plate was then fused in a furnace at 265°C and then tin electroplated a 2nd time. Samples were then rinsed well and submerged in HP-90 for 20 hours.
7	Same as in <u>Table 5</u>.

The rates achieved in the above tests are about 1/4 the rate achieved in the 5 gal container discussed in a previous section but not as low as desired. Additional plating of the tin lined 5 gal vessels will be performed in order to obtain this improvement. Plating of an aluminum container will also be attempted.

Plastic Linings

A few experimental bag liners for 5 gal containers have been made of Aclar 33c film by sealing the edges with a Robot strip sealer and then heating with a hot air gun in order to make the corner folds necessary in order to fit the cylindrical vessel. The top lip seal was also made by heating and stretching the plastic to fit the container rim. The high degree of crystallinity of the Aclar 33c film causes formation of corner cracks in the bag as these manipulations are performed unless the film is properly heated before forming. Care must also be used to avoid flexing of the liner after it is placed in the container otherwise leaks in the film may be developed. The less crystalline grade 22A film may be less susceptible to this type of breaking.

The 5 gal vessels will be lined and filled as they are needed in the program.

Program

Apparatus will be constructed in order to apply the ion exchange procedure to 5 gal quantities of HP. Provision will be made for the use of two beds in series in order that this larger scale test might be compared with the laboratory tests.

A laboratory distillation unit will be completed and used for preparing 90-98% HP. When test samples show sufficient cleanliness of the unit the 5 gal storage samples will be made.

Tin lined 5 gal vessels previously used and an aluminum vessel will be tin electroplated in order to prepare vessels for storage samples.

Vessels of aluminum lined with Aclar bags will be used for several of the demonstration samples in addition to the few which will be stored in glass. Both Aclar and glass will be used in order to minimize the effect of the heterogeneous decomposition on the storage sample and the interpretation of the results.

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13. ABSTRACT

Investigation of means for reducing the rate of decomposition of concentrated HP by removing the catalytic elements carried in the HP and by reducing the catalytic activity of the various materials of construction for use as containers has been continued.

For aluminum alloys various chemical treatments have not surpassed the caustic-nitric acid - hot concentrated HP sequence in achieving minimum surface activity. For stainless steel alloys only minor changes in surface activity have been achieved by chemical pretreatment. For both types of alloys the chemical composition is a primary factor governing surface activity.

Various combinations of inorganic ion-exchange media have not proved to be more effective than β-stannic acid alone in reducing the decomposition rate of the treated HP. Evaluation of HP-90 which had been treated by β-stannic acid bed and stored in aluminum for approximately 1 year showed the HP to have about 1/3 the decomposition rate of the untreated feedstock.

Activities of tin surfaces electroplated onto aluminum have been shown to be several times higher than the best tin surface or the best passivated aluminum surface.

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KEY WORDS

Storable Concentrated Hydrogen Peroxide
Purification
Ion Exchange
Stabilization
Surface Activity Tests
Safety Tests
Container Linings
Decomposition Rates