Storable Concentrated Hydrogen Peroxide

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FRPL-TR-66-207

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

Contract No. AF 04(611)-11416

Quarterly Progress Report No. 1 March - May, 1966

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FOREYORD

This report describes research being carried out to improve the storability of concentrated hydrogen perc ide. 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 report describes the work carried out by Shell Development Company, Emeryville, California in the period of March 1, 1966 - May 31, 1966.

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

> Forrest S. Forbes Chief, Liquid Propellant Branch

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ABSTRACT

Extension of current interest is bipropellant systems using concentrated hydrogen peroxide as oxidizer requires the development of the capability of storing the peroxide in sealed containers for several years duration. Controlling the pressure buildup in such sealed containers over so long a period of time requires high purification of the peroxide by removal of trace quantities of metallic contaminants and requires container surfaces of very low catalytic activity toward decomposing the peroxide.

The methods of purification involving ion exchange over insoluble inorganic materials, redistillation and recrystallization examined in some detail under a previous investigation are being continued and extended in the present study in order to achieve the optimum improvement in stability. Additional study of means of preparing inactive surfaces through tin electroplating techniques is also being pursued. Demonstration samples of five-gallow size of concentrated hydrogen peroxide prepared by the means developed and emelosed in vessels of pyrer or with ACLAR plastic or electroplated tin linking will be prepared at a later date and stored at ambient temperature for observation. Similarly prepared samples from a previous investigation have been and will be continued in storage in order to observe the effects of storage time on the contents.

Other materials of construction of interest for systems requiring shorter periods of contact with percuide are being tested for surface activity and for means of passivatica.

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STORABLE CONCENTRATED TYDROCEN PEROXIDE

Introduction

The successful use of concentrated hydrogen peroxide (HP) as a high-energy oxidizer for bipropellant rocket propulsion depends in part on the efficacy of storage of the HP in feed tanks for periods of several years without venting of the decomposition gas. A small finite decomposition can be provided for by means of reasonable ullage and wall strength but, as discussed in detail in a previous investigation,^a) for storage of several years duration it is imperative that decomposition rates for HP be reduced by nearly one order of magnitude below those currently attainable in commercial HP and that the most inert surfaces be used on containers for the HP in order that the required ullage and wall strength of the vessels be reasonable.

As described in the previous study^{a)} the decomposition of HP is considered as the result of five different reactions with emphasis in the present study being confined to the first three. Thus, this investigation will be concerned with 1) the so-called homogeneous decomposition occurring in the liquid phase and the heterogeneous decompositions occurring 2) at the liquid-surface interface, and 3) at the vapor-surface interface. The total observed decomposition will be considered as the sum of these three assumed first order reactions:

$$\frac{d (HP)}{(HP) dt} = D_1 + D_2 + D_3 = k_1 + k_2 \frac{S}{V} + k_3 \frac{S}{V}$$

where (HP) represents the concentration of HP, t represents time, S represents the submerged surface area of the container, s represents the non-subserged surface area of the container, V represents the volume of the HP, D represents the part of the total decomposition and k the specific rate constant for the assumed first order reaction with the subscripts 1, 2 and 3 referring respectively to the three reactions noted above. With surface areas in square centimeters, volumes in cubic centimeters and time in either days (for 100°C measurements) or years (for 25°C measurements) the decomposition will be expressed in fraction per day (day^{-1}) or per year $(year^{-1})$ with the units for k_1 being day⁻¹ and for k_2 and k_3 being centimeter/day (or year⁻¹ as the case may be). It is understood that values of k_1 , k_2 and k_3 are specific for specific temperatures and can probably be extrapolated to other temperatures from O to 150°C by means of an Arrhenius activation energy of 18 kcal/mole. It is also understood that values of k_1 vary greatly with variations in metallic ion or stabilizer content and that values of k_2 and k_3 vary significantly with chemical treatment of the surface.

 a) Monger, J. M., "Concentrated Storable Hydrogen Peroxide," ARPA Contract DA-04-200-AMC-569(Z); Quarterly Technical Summary Reports No. 1 (May-July 1964), No. 2 (August-October 1964), No. 3(November-January 1965) and No. 4 (February-April 1965); Final Report, May 1964-August 1965, to be issued. いて、新聞、天日とう時代の法を見た

The assumption made above that these reactions behave as first order reactions can be used safely where very small changes in concentration of the HP occur. However, in comparing the surface activity of a material in contact with HP-90 as against that in contact with HP-98 this assumption may not be correct. As measurements are obtained this possibility will be checked.

In addition to the aim of attaining long term storagability some effort is to be expended in measurements useful for short term contact with HP on various materials of construction. Surface activity measurements will be made in order that gas pressure buildup in systems using these materials might be predicted with a fair degree of accuracy. Results on a few of these materials will be compared to measurements made earlier⁴/ at temperatures up to 200°C by a dynamic method.

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 five years might be feasible.

The scope of the investigation will be:

1. to continue laboratory investigation of ion exchange, distillation and recrystallization techniques of 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 five 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.

a) Hood, G. C., Monger, J. M., and Sanborn, C. E., "Thermal Stability of 90% Hydrogen Peroxide", Navy Contract NOas 56-1023-d, Final Report July 1956.

Observation of Previously Stored Samples

A group of 18 samples of various HP-stabilizer combinations or HP-container combinations are still in storage at 25° C from a previous study^a) and have been monitored since the end of that contract in order to evaluate the combinations over a longer period of time. Of these, 14 have now been uder observation for 8,000-10,000 hours. The progress of these samples is shown in <u>Table 1</u> and <u>Figures 1</u> and <u>2</u>.

Table 1. DECOPPOSITION OF HP-90 IN FIVE-GALLON CONTAINERS

Samp. No.	HP-90 Source	Container Surface	Na ₂ Sn(OII) ₆ a) 10 ⁶ x m/1	Storage Days	Decomposition Overall, year ⁻¹	S/V cm ⁻¹
1013B 1001 1005 1007 1006 1004 1017 1018	Shell Chem """" """" """"""""""""""""""""""""""	Pyrex 1260 A1 """ """ """ """ """	35 0 0 8.8 39 37 ⁰) 37	384 476 455 451 465 399 379 360	0.00031 0.0091 0.0080 0.0078 0.0046 0.0020 0.0019 0.0024 0.0054	0.197 0.198 0.203 0.204 0.200 0.201 0.205 0.206 0.206
1002 1003 1022 1019B 1012B 1016 1010 1011 1023B 1024	Electroly- tic """""""""""""""""""""""""""""""""""	" " Pyrex ^e) 5052 Al " " Kel-F " " Electrolytic Tin ^f) " "	20 107 36 36 36 36 47°) 36 36 36 34 34	442 325 378 385 409 466 466 259 330	0.0057 0.0045 0.0026 0.0026 0.0025 0.0023 0.0022 0.0022 0.0040 0.0138	0.202 0.199 0.220 0.205 0.201 0.212 0.218 0.215 0.204

a) Nitric acid also added to give direct reading pH ca 0.3.

b) Cyclohexanediamine tetraacetic acid added $(3.3 \times 10^{-6} \text{m/l})$ to protect and aid the stannate.

c) 8-Hedroxyquinaldine added (5.4 x 10^{-6} m/1) to protect and aid the stannate.

a) Treated with stannic acid ion exchanger.

e) Transferred from a 1260 aluminum container after 52 days.

f) Tin plated over fused tin surface by stannous sulfate-sulfuric acid process in these laboratories.

a) Monger, J. M. "Concentrated Storable Hydrogen Peroxide", ARPA Contract DA-04-200-AMC-569 (2); Final Report May 1964-August 1965, to be issued.

(Figures 1-2 follow)



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The three unstabilized samples show an apparent gradual decrease in rate during the first 0.8 year with evidence of an increase during the succeeding 0.4 year period. The former might be caused by a gradual passivation of the aluminum surface in contact with the HP, through formation of a deeper layer of oxide. The latter may be due to a gradual pickup of metallic contaminants from the metal surface which, in absence of stabilizer, will increase the homogeneous decomposition rate. Some contamination may have occurred at this time by condensate draining back into the sample from the gas delivery tube (type 5050 aluminum) since air temperature of 12-15°C (below the 25°C temperature of the sample) were experienced for several days during this period.

The two stabilized samples of electrolytic HP-90 (in 1260 aluminum) also show a gradual decrease in rate over the first 0.8 year with a slight reversal thereafter. Gradual passivation of the surface may be responsible for the decrease. The increase due to pick p of contaminants from the container or tubing would be less than that in the previous samples due to the presence of stabilizer.

Two samples of non-electrolytic HP-90 (in type 1260 aluminum) stabilized with about 37 x 10^{-6} m/1 of stannate (4.4 mg/1 as tin) show steady increase over the 1.2 year period until the present rate is about 1.7 times the initial rate. A gradual increase in contamination from the vessel wall or ε gradual deactivation of stabilizer might explain this rise.

One sample of non-electrolytic HP-90 (in type 1260 aluminum) stabilized with about 9 x 10^{-6} m/1 of stannate (1.0 mg/l as tin) has shown a large steady increase in rate until the present time. The rate is now equivalent to that of the unstabilized HP-90. Whether the explanation is that the tin has become ineffective due to precipitation as an aluminum-tin complex or whether greater contamination of this sample has occurred through pickup from the vessel walls or through other means cannot be determined without opening and analyzing the sample. This is planned for the f ture.

The one sample of non-electrolytic HP-90 stored in pyrex and stabilized with 35 x 10^{-6} m/l of stannate (4.1 mg/l a tin) has shown essentially a constant rate of decomposition throughout the 1.2 years of storage, with the exception of two short periods (at about 0.6 and 0.7 year) when cold dir temperatures may have caused condensation of HP in the gas delivery tubes. There heterogeneous decomposition of the condensate on the type 5050 aluminum tubing surface may have accounted for the short spurts or condensate drain-back into the sample may have caused increased homogeneous decomposition before being sufficiently stabilized by complexing with the stannate. The fact that the present rate is apparently no different from the earlier rate would tend to support the just hypothesis. The stabilized non-electrolytic HP-90 stored in Hel-F lined vessels has shown essentially a constant rate of decomposition with the indication of a very slight decrease in the first 0.4 year. Agreement between the two samples has been very consistent.

The two stabilized samples stored in type 5052 aluminum have both shown a consistent rise in rate of decomposition indicating an increase in contamination but otherwise differ with each other by nearly a factor of two. Without further analytical evidence it can only be assumed at this point that the difference is due to imperfect cleaning of the sample container.

Two samples stored in tin plated vessels differ by more than a factor of 3. These vessels have a prior history of plating and testing^a) but most recently were both electroplated by the stannous sulfate-sulfuric acid technique in these laboratories. The best sample (No. 1023B) shows a rate comparable with the best in type 5052 aluminum (No. 1012B) but nearly double the rate in type 1260 aluminum. To date no improvement with time due to increased tin content is apparent.

Three samples of HP-90 were treated by passing through a bed of stannic acid for removal of contaminants by ion exchange prior to being stored in type 1260 aluminum vessels. Of these one was non-electrolytic IP-90 (No. 1018) which, after a short initial rise in rate, has remained fairly constant at a rate similar to the two non-electrolytic samples in 1.260 aluminum described above. One sample of electrolytic HP-90 (No. 1022) is also of decomposition rate similar to two untreated samples but may be increasing slightly. The third was also electrolytic HP-90 (No. 1019B) and was first stored in type 1260 aluminum (the same vessel later used ior sample No. 1022) for 0.14 year and then transferred to pyrex. None of these results show that improvement has been achieved by this particular bed treatment. Since these samples are completely at odds with results obtained at 100°C from laboratory samples passed through this same bed no explanation is offered at this time. The latter sample has given data showing that the aluminum vessel walls are of con iderably higher surface activity than predicted from leboratory tests on 1260 aluminum strips.

Purification of HP

Ion Exchange

The use of insoluble inorganic material having numerous hydroxyl groups as potential ion exchange sites, or having multivalent elements such as tin incorporated in their structure as potential complex formation sites, showed significant promise in earlier experiments as a means of removing contaminant ions from concentrated HP. Of the common methods of

a) Monger, J. M., "Concentrated Storable Hydrogen Peroxide", ARPA Contract DA-O^h-200-AMC-569 (Z); Final Report May 1964-August 1965, to be issued. purification this appeared most attractive as an on-loading procedure because of its simplicity and because theoretically those contaminants picked up in transit or in handling could also be removed. However, the preliminary testing has indicated that a combination of such ion exchange media may be necessary, rather than a single medium, in order to achieve the degree of purification sought.

Tests of several different compounds as ion exchangers for concentrated HP have been initiated and a few results of these tests, both of single compounds and combinations, are given in <u>Table 2</u>. For comparison and evaluation of the treatment the decomposition rates of some of the feedstocks used and their response to stannate stabilizer are shown in Figure 3. Several of these exchangers are beds previously used and the tests were performed in order to check the values obtained with those previously observed. Those so tested, alpha and beta stannic acid, aluminostannic acid and dried aluminum hydroxide, gave results very similar to those previously obtained.

Tests with electrolytic HP-90 over the previously used alphastannic acid bed did not show a great amount of improvement in stability. Since this bed had been used for over 1200 bed volumes, and with HP loaded with aluminum ion, it was regenerated by washing it with 5% ammonium hydroxide. Following this it was used for treating a sample of DuPont HP-90 and then for treating the electrolytic feedstock HP-90 again. Neither of these samples was significantly improved in stability over their initial values. It would appear that the 5% ammonium hydroxide regeneration was not sufficient to return these solids to their original condition.

The beta-stannic acid solids reduced the decomposition rate of the sample of electrolytic HP-90 used to about one-third of the original and further stabilization reduced it to 0.0015 day⁻¹ at 100°C. These values were very similar to those obtained with the HP used to pre-test the sample flasks and suggest that, of the latter decomposition rate, approximately 0.0006 day⁻¹ may have been due to the heterogeneous decomposition on the vessel walls leaving approximately 0.0009 day⁻¹ as the homogeneous decomposition. This would be approximately 0.1 the original decomposition rate of this particular feedstock.

A sample of DuPont HP-90 was then passed through this bed in order to determine the effect on the stability of this HP. As shown in the table the decomposition rate of the effluent was about the same as that of the previous effluent but only marginally better than that of the feedstock.

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(Table 2 and Figure 3 follow)

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

					ورجية مستقدية وتعادينها والمتقاطعة	المحاوية والحراب موجود والمختلف ومحاله الم		A REAL PROPERTY AND A REAL	
Ref. No.	Bed S	Size ^e)	Ef Acc	fluent umulati	ve	Samp.	pH ^c)	Decompo day 1	at 100°C
с) 	cc	1/d	ml	Bed Vols.	LHSV ^b)	1.0 •		Unstabil- ized	Stabilized
	With	Alpha	-Stanni	c Acid	Solids,	2£)			
9796 -	6.7	8.5	8900	1328	36.	38	0.46	0.0046	0.0036
g)h) g)			9750 9800 10050	1455 1463 1500	16.	82 83 84	1.33 1.33 1.39	0.0037 0.0033 0.0058	0.0032 0.0020 -
	With	Beta-	Stannic	Acid S	olids,	2	A.		
9796-	6.0	7.5	2700	450	7.2	40	0.79	0.0035	0.0015
g)			2900	483	6.2	85	0.12	0.0030	-
	With	Dasic	Stanni	c Phosp	hate So	lids, l			
9796 - 11	9•5	1.1	900	95	6.0	51	2.48	0.0056	0,0052
	With	Acidi	c Stann	ic Phos	phate S	olids ⁱ⁾ ,	1		
97 96-	77	2.3	350	45	10.4	66	0.29	0.0044	0.0040
14			550	71	13.0	65	0.36	0.0046	0.0043
	With	n Basic	and A.c	idic St	annic P	hosphate	Beds in	Series	
9796 -	9.5,	1.1,	500	65j)	17.3 ^j	70	0.21	0.0050	0.0044
14		2.)	700	91	11.1	69	-0.28	0.0052	0.0048
	Vith	n Basic	Stanni	c Phosp	hate an	d Beta-S	Stannic Ac	id in Series ¹	()
9796-	9.5,	1.1,	350	35j)	6.7 ^{j)}	78	1.38	0.0064	-
g) TO	10.0	2.0	400 800 850	40 80 85	6.7 8.6 8.6	79 81 80	1.38 1.30 1.30	0.0061 0.0038 0.0060	0.0036 0.0056
	Vitl	n Acidi	e Stann	ic Phos	phate a	nd Alphe	-Stannic	Acid in Serie	98
9796-	7.7,	2.3,	350	52j)	16.3 ^j)	86	1.17	0.0051	940
1 1 1	0.1	2.0	500	75	30.0	87	1.18	0.0069	-

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(Table 2. Contd.) DECOMPOSITION RATES OF ION EXCHANGE EFFLUENT AT 100°C

Pef. No.	Bed Size ^{a)}		Effluent Accumulative			Samp.	pH ^c)	De compo dav	esitiond) at 100°C		
e)	cc	1/d	ml	Bed Vols.	LHSVD)			Unstabil- ized	Stabilized		
	With	Alumin	o-Stan	nic Aci	id Solida						
9796 12	15	10.	1250	83	10.0	54	0.37	0.0031	0.0023		
	With	Mole S	eive 5	A, Unbo	onded		<u></u>				
9796- 13	13	10	500	3 8	6.6	53	2.18	0.0061	0.005%		
	Vith	Dried	Alumin	ım Hydı	roxide						
9796- 10	7.5	5.2	5800	774	13.3	3 9	0.80	0.0020	0.0021		
a) P	od siz ratio expan	e measu of len ds at t	gth to the both	t with diamet tom nea	HP-90 an ter, and ar the in	d, ther is appr let fil	efore, ex oximate s ter.	panded . 1/d : since the bed of	ls the liameter		
b) 1 c) 1	 b) Liquid hourly space velocity in terms of bed volumes per hour. c) Direct reading with glass-calomel cells. When over 0.8 the pH was reduced to approx. 0.3 with HNO3 before measuring the decomposition rate. 										
d) V	alues	uncorre	cted for	or cont	tribution	by the	vessel v	alls. Pretes	ts indicate		

approximately 0.0006 to 0.0012 day⁻¹ may be due to the vessel wall. Stabilized values are with about 34×10^{-6} m/l stannate added.

e) Becco electrolytic HP-90 used for feed unless otherwise noted.

Solids previously used with HP-90 preloaded with Al⁺⁺⁺ at 40 X10⁻⁶ m/1. **f**)

g) DuPont non-electrolytic HP-90 used for feed.

Solids washed with 5% 10H40H and then with deionized distilled water. h)

i) Stannic phosphate solids washed with 15 HHO3 and then with water. Mater effluent pH was 2.7 after 120 bed volumes.

j) Based on the second bed in the series.

k) Beta-stannic acid solids regenerated by washing with 5, NH_OH followed by washing with 1, HNO3 followed by washing with deionized distilled water until pH of effluent water was 5.



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Stannic phosphate solids, prepared by precipitation from a mixture of sodium stannate, phosphoric acid and sodium hydroxide, were tested in two forms: 1) as prepared, giving a basic effluent and 2) after treatment with 12 nitric acid, giving a slightly acidic effluent. Both solids showed very good compatibility with HP-90, giving off very little decomposition gas during use as compared to the other beds used. The effluent from the basic solids was of relatively high pH indicating that exchange for hydroxyl ion may have occurred. Stability, after neutralization with nitric acid, was little better than before treatment, indicating that cation exchange was not significant, unless hydrogen ion were absorbed, or unless the exchanged cations were replaced with soluble or suspended material of nearly equal catalytic activity. Analysis of the effluent showed significant concentrations of phosphorus (1.3 mg/1) indicating that the stannic phosphate is not sufficiently insoluble to use without additional exchanger to remove the phosphorus.

Effluent from the acidic stannic phosphate bed was slightly acidic compared to the feedstock (0.3 compared to 0.8 direct reading) suggesting that some cation exchange for hydrogen ion may have occurred. However, the decomposition ra : of the effluent was only reduced to half that of the feedstock and showed little response to stannate stabilizer. The effluent also showed phosphorus content of 1.9 mg/1, approximately the same as in the previous case.

Since it was obvious that neither phosphate was satisfactory alone, the two beds were used in series in order to remove, potentially, cations and amons at the same time. The effluent from the basic phosphate bed was passed directly through the acidic phosphate bed and emerged with a slightly acidic pH. The effluent still had a decomposition rate more than half that of the feed and showed little response to stannate stabilizer.

The failure of the combination of basic and acidic phosphates was followed by separation of the beds and recombination of each series with a stannic acid bed, the acidic beta-stannic acid following the basic phosphate and the basic alpha-stannic acid following the acidic phosphate bed. In both cases the pH of the effluent was higher than that of the feedstock requiring neutralization with nitric acid prior to measurement of the decomposition rates. Decomposition rates in both cases were little better than the feedstock. When a second feedstock was used the effluent had a higher decomposition rate than the feed. Since both stannic acid beds had been regenerated after long use the next combinations which will be tried will be the phosphate beds with unused stannic acid beds. Also, as a check, the two regenerated beds will be tried in series with each other.

A bed of alumino-stannic acid solids previously used gave effluent of nearly neutral pH and having a decomposition rate about onethird that of the feedstock. The stability is about the same as that measured before but is still about double the decomposition rate measured in this particular test flask in a pre-test with a sample of better HP-90. The pH is considerably lower than that previously measured on effluent from this bed indicating that acidification has occurred in some manner during storage of the bed.

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A b d of molecular seive 5A, alumino-silicate, without the commonly used clay binders was found to give effluent of fairly high pH (2.2) and with only slightly improved stability. Further testing of this bed is intended, including acid pretreatment.

A bed of dried aluminum hydroxide (hydrated alumina) which had been used previously with HP-90 containing a small amount of sodium hydroxide, thereby raising the pH of the effluent up to near neutral, gave effluent with a pH similar to the feedstock now used and with a decomposition rate of 0.0020 day⁻¹. Addition of stannate stabilizer did not improve the stability, which was better than the original for this feedstock but not as good as the pre-test sample measured in the same test flask. Analysis of the effluent showed aluminum, dissolved or suspended, had been picked up to a concentration of 0.17 mg/l. A series combination of this bed with a beta-stannic acid bed 1. intended for future study.

Distillation

Another means of purification which has been shown in past studies to give HP of exceptional stability is flash distillation. Although previous tests indicate that a significant homogeneous decomposi tion rate still persists after distillation, due perhaps to contaminants picked up from the walls of the still lines or the test vessel or due to partial vaporization of impurities in the feed, uncertainty of the amount of heterogeneous decomposition which may have occurred on the walls of the test vessel leaves doubt as to the real magnitude of the homogeneous decomposition. In order to define this more clearly additional experiments must be made with redistilled HP with varied surface to volume ratios in a given test apparatus and with reduced surface to volume ratio. The latter can only be obtained by testing larger volumes of sample in large containers. This means that a distillation apparatus capable of producing samples of two orders of magnitude larger than previously used will be needed so that test samples as well as storage samples can be produced.

Apparatus made of pyrex has been designed and parts have been constructed in order that such a distillation may be carried out in continuous manner under remote control. Because of the potential vapor explosions possible the distillation will be performed at reduced pressure in order that temperatures above 60°C can be avoided. Also, in order to achieve low pressures, the vapor will not be passed through distillation plates but will be passed through a partial condenser, thereby acheiving a condensate of higher concentration. Additional safety features will be a self-leveling feed reservoir to supply a significant volume to the reboiler in order to prevent the reboiler going dry, and a constant bleedstream from the reboiler to a diluent water stream in order to prevent large buildup of hazardous materials in the bottoms. さいろうないないないないないないないないないないないないない 日本のできたいろう

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Assembly of the parts is continuing and construction of the apparatus will be started when the lemanded by other items of investigation lessens.

Studies of Container Surfaces

Of equal importance to stable HP in obtaining Yow decomposition and pressure buildup during long term storage is the selection of materials having very low catalytic activity toward HP and which do not contribute contaminants for use in constructing container vessels. For vessels of small to moderate size having relatively large surface to volume ratios only the most inactive surfaces would yield less decomposition than that homogeneously decomposed (assuming the most stable HP is used). For these surfaces the most promising by laboratory test have been fluoro- and fluorohalo-carbon plastics, "pure" electrolytic tin and "pure" aluminum.

A variety of the commercial fluoro- and fluorohalo-carbon plastics are available with potentially individual reactivities toward HP. These are being tested with HP in an attempt to select the least catalytic one for further stur, if real differences exist between them. Since some of these are not c pletely halogenated and since their potential explosive reaction with HP-98 has not been thoroughly explored, a few precautionary safety tests with HP have been made. These are described in a following section.

The surface activities measured to date are also given in a following section and include those made on several materials which will be of interest only for short term contact with HP. These will be of interest in calculating the prossure buildup in some systems where short term contact is planned.

The potential passive nature of pure tin and its possible application as a plated coating on vessels of aluminum or stainless steel has prompted continued exploration of electrolytic plating by various procedures with checks on the catalytic activity of the resultant surfaces toward HP. The current results are also given in a following section.

Safety Tests

Although considerable testing has been done previously on the plastics of interest in this study with HP-90 a relatively smaller amount has been done with HP-98. Since tests of surface activity on these materials were scheduled for 100°C and with HP-98 a few simple tests of explodability of these plastics with HP-98 were run. The results are shown in <u>Table 3</u>. Included in the test program also was some polyvinyl chloride tubing and Kel-F-90 grease intended for laboratory uses with HP.

The impact test was performed with a drop-weight tester giving an impact of 70 kilogram continuetors over a piston area of 0.46 cm². This tester was of similar design to one used previously on testing HP-90 with soluble organics" and with shredded plastic.^b) In the present tests the plastic was cut into thin shavings or was a thin film shredded into thin fibers in order to obtain a reasonable amount of surface without much bulk volume. None of these impact tests were positive although polyvinyl chloride filings gave a positive test in a previous investigation.^D) The difference is assumed to be the relative surface area of the polyvinyl chloride filings and the lack of volume of plastic which might have acted as a mild heat sink to absorb part of the energy.

Material	Impact	Boiling	Vaporized
	Test	HP Test	HP Test
Teflon TFE Teflon FEP Aclar-33C Aclar-22A Kel-F-800 Kynar Myon ^a) tubing Flexigon ^a) tubing Kel-F-90 grease	Negative n u u n n u u	Negative n n n n n n n n	Flammable b) Flammable c) Flammable c) " " flammable d) Flammable d) Flammable e) Flammable f)

Tal	ble	3.	SAFE	IY TE	ST	RESULTS	,
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a) Polyvinyl chloride, plasticizea.

b) Yellow-white flame.

c) White flame.

d) Yellow-white flare with considerable soot; leaves carbon ash.

e) White flame with vigorous burning and considerable gassing. Flame continues in absence of HP vapor.

f) White flame. Partial vaporization at temperature of test.

The second test performed was to heat the HP-98 rapidly to above the boiling point while in contact with the plastic. A small volume (0.2 cc) of HP-98 was heated in a beaker from room temperature to the boiling point in four minutes and evaporated to dryness in another two minutes in contact with film-like shavings of the plastics, or a smear of the Kel-F grease. None of these tests showed evidence of reaction.

a) Monger, J. M., Sello, H., and Lehwalder, D. C., Chemical Engineering Data 6, 23 (1961).

b) Hood, G. C., Monger, J. M., and Sanborn, C. E., "Thermal Stability of 90% Hydrogen Peroxide", Contract NOas 56-1023-d, Final Report July 1957-June 1958.

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The third test consisted of dropping small amounts of HP-98 into a preheated peaker containing shreds of the plastic or a small smear and globule of Kel-F grease. The temperature of the beaker was opproximately 200°C and the plastic became heated to this temperature also within a few seconds after adding. The small additions of HP-98 boiled and vaporized rapidly, frequently yielding small, non-destructive vapor explosions. All of the plastics burned in the HP-vapor, with a heat and vigor somewhat dependent on the degree of saturation with fluorine, with tetrafluoroethylene Teflon burning least sigorously and with a yellowish flame. The fluoroethylpropylene Teflon, Aclar and Kel-F burned with a white flame only while HP vapor was in shundance, in the same manner as Taflow TFE. Kynar burned vigorously giving off considerable soot and smoke and tended to continue burning momentarily after dissipation of the HP vapor. A carbon ash remained near the end of the experiment out this too was consumed with more HP. The two tubing samples, thought to be polyvinyl chloride plastic, burned with considerable vigor and with considerable generation of gas of unknown composition. The flame continued in the absence of HP vapor. Kel-F grease, used on laboratory glass joints, burned in a manner similar to Kel-F film except that some vaporization was apparent on first heating. This vapor could conceivably be mixed with HP-oxygen vapor to bring about a vapor explosion but did not in the several tests performed.

None of the above tests resulted in an explosion. Since several of these materials were near their melting point they flowed over the surface of the beaker during the test. However, the viscosity was high and the immiscible liquid - HP liquid type mixture, which has investigations in other systems, ²) did not occur. It is conceivable that with sufficient bulk of plastic and sustained heating of HP that burning might result in the superheating of the plastic to a point where fluidity as well as vapor formation could lead to HP - organic explosion. For practical purposes, however, the above plastics are considered to be safe for the intended usage in these investigations.

Surface Activities

The catalytic activity of a particular surface, especially the metal surfaces, toward decomposing HP is dependent on the elemental composition and to some extent on the chemical state of these elements. With aluminum alloys, the primary surface exposed to HP is aluminum oxide or hydrated oxide with various fractions of contaminant metals such as iron, copper, chromium, manganese and others with various catalytic activities. The aluminum oxide has a different catalytic activity also depending on whether it has been treated with strongly basic or acidic solutions, and will change also with continued contact with hot HP. Therefore the initial catalytic activity measured in HP will be characteristic of the alloy and its previous preparation treatment. With continued long term contact with hot HP a steady state activity is approached which is characteristic of the alloy but less dependent on the previous chemical treatment, except where the chemical treatment may have altered the elemental composition on the surface.

a) Hood, G. C., Monger, J. M., and Sanborn, C. E., "Thermal Stability of 90% Hydrogen Percxide", Contract NOas 56-1023-d, Final Report July 1957-June 1958. 5**64**5

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With stainless steel alloys the activity is probably a complex function of the elemental composition of the surface, the state of oxidation resulting from its chemical bonding during formation and the state of oxidation resulting from its chemical preparation treatment. Agein long term contact with hot HP will probably result in an activity dependent on the chemical composition of the alloy rather than pretreatment.

The procedures for treating the surfaces prior to measurement of the catalytic activity are given in <u>Table 4</u> and consist of solvent degreasing, caustic wash to remove surface oxides and nitric acid wash to remove some metallic elements and form an oxidized surface. Other chemical treatments will be tried in future experiments.

	Table 4.	DESCRIPTION OF SURFACE PREPARATION
Treatment No.		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 temperature.
3.		Sample submerged in 10% NaOH for 16 hours at room temperature.
4.		Sample submerged in 1% HNO3 for 5 minutes at room temperature.
5.		Sample submerged in 35% HNO3 for 16 hours at room temperature.
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.
- Feeb anos	dumo to f	allound by thorough minging in deionized

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

Several aluminum alloys which are of interest in various systems have been tested at 100°C and the results are given in <u>Table 5</u>. Evaloying an Arrhenius type activation energy of 18 kcal to extrapolate to other temperatures would give values 1/400 those listed for activities at 25°C. Two plastics, Aclar 22-A and Kynar, have also been tested and are included in the table. The initial measurement made was after only a solvent degreasing treatment and presumably would give the highest catalytic activity depending on the amount of imbedded contaminant or the のないので、「「「「」」

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absorbed contamination. The second measurement recorded was after 10 to 30 hours of contact with HP-90, with frequent represent of the HP-90, in order to prepare an oxidized surface and to remove any dissolved elements. A similar set of measurements was made after first giving the metal sample a caustic and acid pretreatment.

Samla	UD	Sur	face	c/w	Decompos	ition Ra	te	
No.	No.c)	Type	Preparation ^{a)}	cm ⁻¹	Overall day ⁻¹	Blank ^{b)} day-1	k₂ cm∕day	
19 19 19 36 " 2 " 18 " 25 " 17 " 24 " 20 " 37 " 21 " 23 " 77 " 60 "	A18-2 "" A18-2 "" A18-2 "" A18-2 "" A18-2 "" A18-2 "" A18-2 "" A18-2 "" A18-2 "" A18-2	1260 A1 """ 1100 A1 """ 5052 A1 """ 5052 A1 """ 6061 A1 """ 6053 A1 ^d) """ 5053 A1 ^d) """ """ Aclar-22A """ Kynar	$ \begin{array}{c} 1 \\ 1,7 \\ 1,2,5,6 \\ 1,2,5 \\ 1,2,5 \\ 1,2,5 \\ 1,2,5 \\ 1,2 \\ 1,2 \\ 1,2 \\ $	1.77 2.06 1.42 2.07 1.981 1.98 2.01 2.02 2.0331 2.644 1.65766 1.6746 1.6356 1.63566 1.63566 1.63566 1.63566 1.635	0.148 0.0082 0.0127 0.0066 0.766 0.098 0.0383 0.0108 1.83 0.424 0.0522 0.0124 0.770 0.077 0.0374 0.0060 0.0900 0.0095 0.0608 0.0154 0.143 0.0075 0.0549 0.0150 0.0089 0.0055 0.498 0.0437	0.0055 0.0052 0.0010 0.0032 0.005 0.021 0.0035 0.0076 0.006 0.0137 0.0041 0.0065 0.0042 0.0070 0.0042 0.0055 0.0042 0.0055 0.0055 0.0056 0.0055 0.0050 0.0055 0.0050 0.0055 0.0056 0.0055 0.0056 0.0056 0.0056 0.0056 0.0055 0.0055 0.0056 0.0055 0.0055 0.00056 0.0055 0.0056 0.0055 0.0056 0.0056 0.0055 0.0056 0.0050 0.0056 0.0056 0.0056 0.0050 0.0056 0.0056 0.0050 0.0056 0.00500000000	0.080 0.0015 0.0082 0.0016 0.420 0.039 0.024 0.0015 0.905 0.145 0.024 0.0020 0.422 0.024 0.0020 0.422 0.024 0.0020 0.422 0.024 0.0032 0.0009 0.063 0.0005 0.0013 0.0005 0.0013 0.0005 0.074 0.0065	
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Table 5. SURFACE ACTIVITIES IN STABILIZED HP AT 100°C

a) Surface preparation according to Table 4.

b) For samples without treatment 7 the blank is determined before addition of the sample. With treatment 7, with repeated replacement of the HP-90, the blank is determined after test and removal of the sample. The blank includes the homogeneous decompost ion by contaminants and the heterogeneous decomposition due to the vossel wall, including any contaminants absorbed there.

c) HP-90 from drum Al8 with Na₂Sn(OH)₈ at 34x10⁻⁸ m/1 and HNO₃ at 69x10⁻⁸ m/1 added as stabilizers.

d) This alloy is the cladding on 2014 aluminum sheet. The sample includes a thin edge surface of 2014 aluminum.

e) The initial blank is used here since the final post-test blank was higher than the overall measurement, due to copper contamination.

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f) This alloy is the cladding on 2219 aluminum sheet. The sample includes a thin edge surface of 2219 aluminum.

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In several cases this pretreatment reduced the initially measured activity by a factor of 10 or more. The final weasurement was also reduced in some cases by this pretreatment but not in others. The length of time required to reach the final lower catalytic activity by contact with hot HP-90 was 20 to 40 hours in all cases.

Pick up of contaminants by the HP-90 during the final approximately 16 hours of the test is indicated by the blank after the reading (after treatment No. 7). When significantly larger than 0.003 to 0.005 day⁻¹ metallic contaminant have been dissolved in the HP and perhaps absorbed on the vessel val... Application of these alloys to a system and anticipation of decomposition rates caused by them would have to be modified by consideration of this latter contamination also.

Similar surface activities after passivation with HP were exhibited by 1260, 1100, 5052, 6061 and 7072 alloys, while the 1260 alloy showed the lower activity with only caustic and acid pretreatment. As stated before, this is probably due to the fact that the 1260 alloy contains the least contaminating metallic elements.

The surface activity of Aclar 22A, without treatment except a simple wash with HP-90, was lower than any of the aluminum samples and confirmed measurements made previously for the more crystalline Aclar 33C.^a) The plastic Kynar appears to be more reactive and in addition is not saturated with fluorine or fluorine-chlorine thereby being potentially more easily oxidized. Although these characteristics are well within the group 1 classification for use with HP it does not appear attractive for long term sealed storage containers.

Surface activity measurements on several of the stainless steel alloys of interest for some systems employing short term contact with HP are given in <u>Table 6</u>. These measurements were made at 80°C because of their relatively active surfaces and the rapid decomposition resulting. Employing an Arrhenius type activation energy of 18 kcal/mole, extrapolation to 25°C would give values about 1/100 those listed for 80°C.

Type 301 stainless steel showed little change by contact with hot HP-90 except to become bronzed in color. Transfer of metal from the sample surface to the vessel wall appeared to take place since the blank increased greatly without apparent change in sample activity. Caustic and acid pretreatment made the surface slightly more active.

Type 304 stainless steel showed significant improvement with continued contact with hot HP. Caustic and r d pretreatment had apparently no effect on the initial activity.

a) Monger, J. M., "Concentrated Storable Hydrogen Peroxide", ARPA Contract DA-04-200-AMC-569 (Z); Final Report May 1964-August 1965, to be issued.

Comia	150	Sur	lace	c /ar	Decomposition Rate				
2.00 TO		Type	Prepara-	0/ V	Overall.	Dienk "	L ₂		
1907 -	140 - 03		tion ^a)	сл –	dev"1	galr	cm/day		
614	A16-2	SS 301-T	1	1.67	0.830	0.0001	0.50		
Ħ	п	11 11	1.7	2.09	1.658	0.399	0.60		
96	п	ya ea	1,3,5,6	1.63	1.216	0.0002	0.75		
H	H	n n	1,3,5,6.7	2.36	1.635	0.203	0.61		
67	A18-2	SS 304	1	1.98	0.926	0.0076	0.46		
ท่	re -	71 71	1,7	2.29	0.721	0.266	0.20		
98	11	78 FF	1,3,5,6	1.59	0.799	0.0002	0.50		
n	11	23 VE	1,3,5,6,7	2.36	1.267	0.112	0.49		
68	A18-2	SS 347	1	1.67	1.261	0.0002	0.76		
n	11) 7 11	1,7	2.48	0.760	0.171	0.24		
93	11	1 1 33	1,3,5,6	1.65	0.458	0.0004	0.27		
11	11	17 ¥1	1,3,5,6,7	2.03	1.145	0.168	0.48		
49	A18-2	SS 17-7	1	2,15	2.265	0.0003	1.05		
· ·		FH				_			
49	t#	RE 11	1,7	2.71	1.223	0.187	0.39		
95	11	15 19	1,3,5,6	1.70	0.805	0.0002	0.47		
11	n	PT 48	1,3,5,6,7	2.29	1.363	0.107	U.55		
94	A18-2	SS AM 350	1,3,5,6	2,16	0.280	0.0003	0.129		
19	118-2		1,3,5,6,7	2,85	0.907	0.084	0.29		
***	ALC-L	78-200	1	1.58	0.150	0.0001	C.095		
13	17	- ii - ii	1,7	2.33	0.128	0.01.05	0.051		
97	81: 	11 11	1,3,5,6	1.65	0.0609	0.0002	0.037		
n	н	ar a	1,3,5,6,7	2.19	0.0747	0.0033	0.033		
50	A18-2	SS Almar	11	2.22	0.215	0.0004	0.097		
ļ		18-250			-	Í			
ŋ	81	TE 19	1,7	2.57	0.181	0.0240	0.051		

Table 6. SURFACE ACTIVITIES IN STABILIZED HP AT 80°C

a) Surface preparation according to <u>Table 4</u>. The treatment with hot HP was for only 1/2 to 2 hour periods and replacement of HP was repeated for only 2 times where only treatment 1 and 7 were employed.

- b) For samples without treatment 7 the blank is determined before addition of the sample. With treatment 7, with repeated replacement of the HP-90, the blank is determined after test and removal of 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 arun Al8 with $\text{MagSn}(OH)_{\Theta}$ at 34×10^{-8} m/l and HNO3 at 69×10^{-6} m/l added as stabilizer.

Type 347 stainless steel also improved significantly with continued contact with hot HP and also showed improvement as a result of the caustic and acid pretreatment. These values are consistent with those measured in these laboratories on freshly prepared 347 stainless steel in a previous investigation.^a

a) Hood, G. C., Monger, J. M. and Sanborn, C. E., "Thermal Stability of 90% Hydrogen Peroxide", Navy Contract MOas 56-1023-4, Final Report July 1956-June 1957.

The precipitation hardened 17-7 steel showed reaction similar to type 347 but with slightly higher rate constant.

Type AM 350 stainless steel gave an initial rate, after caustic and acid treatment, significantly lower than those previously mentioned. Continued contact with hot HP doubled the rate.

Almar 18-200 and 18-250 stainless steels showed surface activities considerably lower than the other samples and, in the one sample tested so far, showed significant improvement after caustic and acid treatment.

Electroplating

Although pure aluminum surface shows an attractively low surface activity toward HP the small amount of pick up of aluminum ion into the HP is detrimental to the life of the stanmate inhibitor and thereby discourages the consideration of pure aluminum for production of very long term storage vessels. Alternatively pure tin surfaces might conceivably maintain a steady state concentration of "soluble" tin, allow continuous precipitation of tin oxide complexes with other impurities and also con ribute a relatively passive surface activity in contact with HP. Unfortunately pure tim is too soft for use as a container unsupported by secondary material. Applying a plated coat of tin to a vessel of high tensile strength has two problems, 1) most materials readily plated by tin are of high catalytic activity toward HP thereby necessitating absolute coverage with no accidental breaks in the film being tolerable and 2) tin dipping or electroplating from the commonly used sodium stannuie bath leave active tin surfaces. Success in preparing an inactive tin surface by electroplating from a stannous sulfate-sulfuric acid bath has encouraged examination of the potential tin plated aluminum surface as a means of avciding the above problems and providing a tin-lined inactive container for Hr storage.

Since the least active base aluminum is desired for the support vessel for the tin plate in order to minimize the contamination and decomposition resulting from an accidential break in the surface film, the preliminary study of electroplating in these laboratories has been with 1260 aluminum. From the standpoint of plating coverage and bonding strength pure aluminum is the most difficult to plate. A compromise procedure is being tried, therefore, by using the well known zincating application of a thin layer of zinc metal over the aluminum prior to tin plating. Any exposed zinc surface would be quickly dissolved and oxidized by HP to the essentially inert zinc ion and the moderately active oxide.

The preparation of the surface prior to electroplating is very critical in achieving a tightly bonded plate. Many of the procedures suggested in the literature^a) are being tried for sample preparation and plating, with the exception that salts or plating of catalytic elements such as copper or iron are being avoided. The most successful

a) Lowenheim, F. A., editor 1963 edition and Gray, A. G, editor 1953 edition, "Modern Electroplating", John Wiley and Sons publishers.

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prosedure to date involves removal of the old aluminum oxide surface by etching in dilute caustic followed by nitric acid wash and then zincating in an 8% zinc oxide-40% sodium hydroxide bath at room temperature. A second zincating step is performed after removal of part of the first plate by dipping in dilute nitric acid. Residual caustic and salts are removed by washing in a very dilute caustic bath followed by washing in deionized water. A final dip in dilute nitric acid is made to neutralize any remaining caustic and then the sample is plated in a 6% stannous sulfate-5% sulfamic acid bath, with the voltage being applied before submerging the aluminum in the plating bath. The sulfamic acid bath appears to give more adherent films than the sulfuric acid bath. Several samples have been prepared in this way, with plating at 0.022 amp/cm^2 (20 amp/sq ft.), with no evidence of blisters and with no peeling of the tin film. However, frequent inconsistent results are obtained which suggest that one or more of the many steps in the process has not been successfully performed. In these cases small blisters raise the tin plate and sizeable portions peel off with mild lifting force. Analyses of these peelings have not been completed so that it is not known which metal bond is at fault.

One set of samples electroplated on tin base metal and one set electroplated on 1260 aluminum were tested with stabilized HP-90 as shown in <u>Table 7</u>. The surface activity of the tin plate appears to be about the same for both sets after some washing with HP. The activity is several times higher than the best previously obtained on electrolytic tin. Additional testing of these surfaces with unstabilized HP is intended since some evidence in previous work indicates a different activity results from contact with stannate inhibitor.

		Surfac	e		Decompo	osition	Rate
Sample No.	HP No.	Type	Prepara- tion ^a)	S/V cm ⁻¹	Overall day ⁻¹	Blank day ⁻¹	k2 cm/day
46	A18-2	Tin on tin	SnSO4-H2SO4	1.65	0.0120	0.0007	0.0068
63	A1.82	Tin on 1260 Al	SinSO4- NH2SO3H	2.33	0.076	0.0040	0.031
63	A18-2	(* 11 11	7	2.82	0.0222	0.0048	0.0061

Table 7. SURFACE ACTIVITY OF TIN PLATED SAMPLES AT 100°C

a) Preparation number, HP and blank determination follow those in <u>5able 5</u>.

Additional experiments are intended also in studying the effects of fusing of the plated surface followed by additional plating. Preliminary experiments indicate that a tighter bond may be formed in this manner.

Plastic Linings

Some of the proposed storage demonstration samples are intended to be stored in Aclar lined vessels, both to obtain a low activity surface to demonstrate the HP stability and to demonstrate the inactivity of the surface. In order to prepare the few experimental bags for the 5-gallon containers some Aclar 33C film of 5 mil thickness has been obtained and experimental seals have been made. With a Robot strip sealer, temperatures of 285-290°C and pressures of 50 psi have given satisfactory seals. The bags, when made, must be placed in the open end vessels and heat-formed over the rim of the vessel in order to be closed by the corner. Teflon fittings and Kel-F tubing will carry the decomposition gas to the measuring device.

Program

Combinations of ion exchangers will be continued to be explored with the standard HP-90 feedstock now in use. Exchangers which show good results will also be tested on HP-98 and other HP-90 feedstocks. Analyses of NH₄OH and HNO₃ washings from used beds are in progress in order to determine which ions are being removed from the HP. Analyses of the effluents are also to be continued in order to determine the amount of the exchanger material carried into the HP and, if possible, to determine the changes in composition of the HP.

The distillation apparatus will be assembled and final cleaning will be performed in preparation for use with HP-90 and HP-98.

Surface activities of the materials now under study or awaiting test will be determined with the standard pre-preparation listed. Other surface preparations are underway. A few materials will be tested with HP-98 in order to determine the effect of HP concentration on the surface activity. A few samples will be tested at temperatures down to 0°C in order to confirm previous evaluation of the temperature coefficient.

Tin plating experiments will explore the feasibility of increasing bond strength by melting the electroplated films and of decreasing activity by replating over the melted films. Some of the other aluminum alloys which do not have high activities will also be tested as base for tin plating, as well as one or two of the steel alloys.

Bag liners for the five-gallon containers will be made and installed in one of the available vessels in order to determine the most practical shape, size and means of sealing the closure at the top opening. When satisfactory methods are decided on, other vessels will be obtained for use with the bag liners.

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KEY WORDS

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

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