HYDROGEN DESORPTION FROM BASE AND PROCESSED PACKAGING ALLOY

by

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ABSTRACT

By the late '80's various microelectronic device manufacturers had experienced the "Hydrogen Phenomenon" knowingly and unknowingly. This phenomenon occurs when residual or absorbed hydrogen has remained within microstructure trap sites of the ferrous alloy packaging materials that they had selected. But as a function of burn-in or other thermal stresses, the hydrogen is desorbed into the cavity of the device. A variety of chemical reactions are then potentially available by which the desorbing hydrogen gas can destroy device integrity and product reliability. To date, a multitude of subsequent chemical reactions have been identified which can be cause for the failure of the product. This paper identifies an in depth analytical routine which has allowed the supplier community to provide the user community with hydrogen free packages. Potential sources or traps for absorbed hydrogen have been theoretically identified. "Bake out" procedures, and the affects of annealing and plating are also reviewed, all of which have been found to ultimately impact device reliability, i.e., should product design and process variables all align contrarily to the needs of the product type in question.

INTRODUCTION:

The phenomenon of Hydrogen Desorption was first observed on captive microwave devices made with Gallium Arsenide die. Titanium adhesion metallurgy also used as in-line resistors were noted to become bumpy and even lose adhesion. Meanwhile the circuits were noted to electrically drift. Residual Gas Analysis (RGA) of this device showed increasing concentrations of hydrogen as a result of thermal stress, e.g., burn-in.

Other device technologies were noted to acquire increasing concentrations of moisture such that in several cases Quality Conformance Inspection (QCI) criteria of Mil-Std-888 Test Method 5008 could not be met. Concurrent with the increase in moisture was the noted increase in hydrogen concentrations. In some cases residual traces of normal air were also noted to change as Argon concentrations remained low, e.g., 100 ppm, but the expected oxygen level at circa 2000 ppm was totally absent.

These incidents all drew their origin from the absorbed hydrogen slowly desorbing into the cavity of the respective devices. Hydride formation with metal systems, such as titanium, and metal oxide reduction, such as the reduction of silver solder glass die attach materials, are now understood to be the root cause for these problems.

IBM personnel set in place a team of industrial participants to help in clarifying the problem. A base metal supplier, packaging houses and an independent analytical facility participated in the study which is detailed in the following paragraphs.

EXPERIMENTAL:

It was deemed imperative that the studies on desorption of hydrogen should have at least two primary factors. First, the study was to be based on alloys and subsequent processes with known, identifiable histories. Secondly, the study was to be statistically significant, in other words, single point occurrences and analysis were not acceptable as credible evidence or data. For this reason often times three to five analyses were prepared from the same sample. With that thought in mind, the reader should be aware, that every "data point" provided in this report is in reality an average of at least three readings or samples.

Base alloys were submitted for analyses in three different thicknesses, 10, 40, and 60 mil. These were selected from U.S. and foreign sources, but their exact identity remained as a blind parameter to the IBM study. The sources of these alloys remained known only to the base alloy supply house.

The procedure for hydrogen desorption and subsequent analysis has been reported earlier in literature and will not be presented in great detail here. Basically, the procedure consisted of sealing known weights of Kovar alloy in pyrex glass ampules in an inert atmosphere of high purity nitrogen. These ampules were then subjected to the desired thermal stress for a given period of time, usually in 200 hour intervals. After which the ampules were submitted for Residual Gas Analyses via the

methods and instrumentation qualified for test method 1018 analyses of Mil-Std-883. After their respective analyses, the samples were then resealed under previously established, controlled conditions into pyrex ampules for the next 200 hour interval of thermal stress. Absolute hydrogen concentrations were verified by the fabrication and testing of ampules with known hydrogen-nitrogen levels as supplied by an independent gas supply facility. A maximum of 2.5% hydrogen in nitrogen was used as a standard. This standard was verified at the beginning of the study and again eighteen months later where the mass spectrometer was found to be able to maintain the quantification of hydrogen in nitrogen to ±5% of the original value.

TASK I. HYDROGEN DESORPTION FROM BASE METAL

Mono atomic hydrogen is the only hydrogen gas species capable of diffusing through metals as an interstitial solute. Hydrogen can be "trapped" in the metal at structural imperfections and incoherent boundaries such as grain boundaries, dislocations, vacancies, micropores, precipitate interfaces, inclusion and particle boundaries. Absorbed hydrogen in excess of the lattice solubility will segregate to trap sites within the metal and increase the total hydrogen solubility by orders of magnitude. Trap site hydrogen can then be desorbed from the metal by thermal aging. Each type of reversible trap site has an associated activation energy for hydrogen diffusion out of the metal and gives rise to strong and weak trap sites. Sources of absorbed hydrogen include; melting processes, acid cleaning, electroplating and electrocleaning, corrosion, hydrogen brazing and annealing, air annealing in humid atmospheres.

The first task measured the quantity of desorbed hydrogen from Kovar sheet stock as a function of time, temperature, and sheet thickness. The tests included several lots from 10, 40, and 60 mil sheet thicknesses. Test coupons were hermetically sealed in pyrex ampules with dry nitrogen and thermally aged as part of a time/temperature matrix. All RGA data was normalized to percent H2 evolved in a 1.0 cc volume from a 1.0 gram sample.

The majority of hydrogen was desorbed in the first 200 hours at temperature with the thicker sheet samples desorbing the greatest amount. Mean percentage values of desorbed hydrogen after 200 hours at $150^\circ C$ were 4.0%, 2.0%, and <0.02% for 60, 40, and 10 mil thick Kovar respectively. Sheet thickness is a dominant factor in the levels of desorbed hydrogen and this may be related to fabrication of the different sheet thicknesses with the 10 mil stock requiring more thermal-mechanical processing, i.e., the fabrication process itself may desorb some hydrogen.

The microstructure of the different Kovar stock thicknesses showed a trend of increasing inclusion density with decreasing sheet thickness. The 10 mil stock has the highest inclusion density and also a finer grain size compared to either the 60 or 40 mil stock. The microstructure may influence the quantity and rate of desorbed hydrogen with higher inclusion and grain boundary densities providing weak trap sites and increased hydrogen flux out of the metal. The cleaner microstructure of the 60 mil and some of the 40 mil stock show the highest desorbed hydrogen levels which may be related to strong trap sites within the grains. There appears to be higher desorption peaks at $150^\circ C$ and $300^\circ C$ for all three thicknesses. These peaks may be due to the type of hydrogen trap sites within the material and their associated activation energies.

There was a slight tarnishing of coupons exposed to $300^\circ C$ which is probably due to oxidation of the Kovar by moisture present in the ampule and may partly account for increased hydrogen levels at that temperature. Water content within the ampules was minimized but difficult to control and no quantitative evaluation of moisture level changes was attempted. For the Kovar alloy (Ni29-Co17-Fe54) at $150^\circ C$ and an assumed water to hydrogen ratio of 50 the oxidation reaction by water is possible. However, this effect is not believed to be dominant since the study showed no correlation with coupon surface area as would be expected if surface oxidation were generating the hydrogen.

Also, it is not thermodynamically possible to directly reduce water to hydrogen and oxygen under the operating test conditions. However, the reverse reaction to form water can take place and it is catalyized by gas absorption on the metal surfaces.

TASK II. OXIDE REDUCTION BY DESORBED HYDROGEN

To demonstrate the mechanism of hydrogen desorption and oxide reduction a matrix was run using copper coupons oxidized to a dark blue-purple appearance. The oxidized copper coupons were sealed in ampules with 60 mil Kovar coupons known to desorb hydrogen. Other test groups were run in parallel to baseline the amount of water initially present and the total amount of desorbed hydrogen from the Kovar coupons. Blank coupons that did not desorb hydrogen were used in the matrix to account for any absorbed water on the coupon surface. After 200 hours at $150^{\circ}C$ the following mean value results were obtained for water and hydrogen.

	SAMPLE	ppm H2	ppm H2O	COMMENTS
A.	Kovar Coupon Blank Coupon	6232	2899	Baseline Hydrogen
B.	Kovar Coupon Oxidized Cu Coupon	5164	4353	Oxide Reduction
C.	Blank Coupon Blank Coupon	ND	2959	Baseline Water
D.	Blank Coupon Oxidized Cu Coupon	ND	3559	No Oxide Reduction

Ampules with the oxidized copper and Kovar coupons visibly showed reduction of the copper oxide layer and after 200 hours the copper was clean. Quantitative RGA data showed that hydrogen levels had decreased and the water levels increased in roughly the same amount which would be consistent with the hydrogen reduction reaction:

$$CuO_2 + H_2 \longrightarrow 2Cu + H_2O, \quad \Delta G^{\circ} (150C) = -87636 \text{ Joules}$$
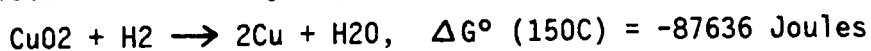
Ampules with the oxidized copper and blank coupons showed no visible oxide reduction and no desorbed hydrogen. This test demonstrates that the sequence of hydrogen desorbing from base metal and subsequent oxide reduction will take place at 150°C. Using the above data for calculations, about 300 anstrons of copper oxide were reduced to produce the observed rise in moisture level.

Other metals whose oxides are able to be reduced by hydrogen include silver, lead, cobalt, nickel, tin, iron, and tungsten. Hydrogen can reduce any available oxide to generate water if it is thermodynamically favorable under the operating conditions. Use of the Gibbs free energy change and the Van't Hoff isotherm will determine the potential for oxide reduction and the equilibrium partial pressure ratio of water and hydrogen. Graphical representation of these reactions with quantitative thermodynamic data are presented in the Ellingham diagram for metal oxides. Using nickel at 150°C as an example, the following equations demonstrate the use of the thermodynamic factors involved.

$NiO + H_2 = Ni + H_2O$
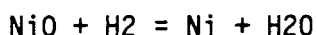
$\Delta G^\circ (150C) = -19935$ Joules $= -RT \ln P(H_2O)/P(H_2)$

$P(H_2O)/P(H_2) = 290$ at Equilibrium; <290 NiO Reduction
>290 Ni Oxidation

AMPULE EXAMPLE: Total Pressure $= 1.0$ atm
99.49% N_2
0.5% H_2O
100 ppm H_2

$P(H_2O)/P(H_2) = 50 < 290 \longrightarrow$ NiO Reduction

$\Delta G (150C) = \Delta G^\circ (150C) + RT \ln P(H_2O)/P(H_2) = -6177$ Joules

Studies with gold over nickel plating showed nickel can diffuse through the gold layer, primarily along grain boundaries, and then spread over the gold surface forming a thin layer of nickel oxide capable of being reduced by hydrogen. Auger surface analysis of plated device packages after burn-in show both nickel and oxygen on the gold surface. Metal hydroxides on surfaces can also react with hydrogen gas to release water and reduce the hydroxide to an oxide. The latter reaction occurs very rapidly and at low temperatures.

TASK III. SURFACE FINISH AND TREATMENT EFFECT

To investigate surface treatment effects used on microelectronic packages a series of Kovar coupons were sent to two different package supply houses for various package treatments and surface finishing. The returned coupons were then sealed in ampules and thermally aged at $150^{\circ}C$. The test matrix included both virgin and hydrogen free coupons prepared by the following supplier treatments:

1. Hydrogen Braze   3. Wet Hydrogen Glass Seal
2. Hydrogen Anneal   4. Hydrogen Bake Out

5. Au Over Ni Plate by Supplier A
6. Au Over Ni Plate by Supplier B

7. Supplier A Process: 8. Supplier B Process:
    i) glass seal   i)   hydrogen anneal
    ii) Au/Ni plate   ii)   hydrogen bake out
                               iii) Au/Ni plate

High temperature brazing in a high concentration H2 forming gas increased the subsequent desorbed hydrogen content of the metal compared to virgin levels, contrarily, low temperature hydrogen annealing in a low concentration H2 atmosphere reduced the desorbed hydrogen content. The glass sealing process in wet hydrogen gas also reduced the desorbed hydrogen content. The hydrogen bake-out process performed by one

supplier reduced hydrogen desorption below detectable levels on all samples processed. Although the bake-out appeared to be effective in reducing hydrogen levels, it is a high temperature process and cannot be used as a final operation after plating because of nickel diffusion to the gold surface causing various attachment problems.

Gold over nickel electroplating and the supplier processes with final electroplating showed inconsistent results. The plating appears to absorb hydrogen into the metal or the plating itself was a source of hydrogen. The plating may also act as a temporary barrier to hydrogen diffusing out of the metal or that hydrogen diffusing from the plating will increase its flux level with longer times at temperature. Further study is required to determine which phenomena are actually occurring and what levels of hydrogen are involved.

CONCLUSIONS:

Microelectronic manufacturers have experienced various device problems related to hydrogen inside the package cavity. This phenomenon occurs when residual or absorbed hydrogen remains within the ferrous alloy packaging materials. As a function of burn-in or other thermal stresses the hydrogen is desorbed into the cavity of the device. A variety of chemical reactions are then potentially available by which the desorbing hydrogen gas can destroy device integrity and product reliability.

The majority of hydrogen was desorbed from Kovar alloy samples in the first 200 hours at temperature with the thicker sheet stock desorbing the greatest amount. Mean percentage values of desorbed hydrogen after 200 hours at $150^{o}C$ were 4.0%, 2.0%, and <0.02% for 60, 40, and 10 mil thick Kovar respectively.

Hydrogen can reduce any available oxide to generate water if it is thermodynamically favorable under the operating conditions. Tests using oxidized copper coupons sealed in ampules with Kovar known to desorb hydrogen showed complete reduction of the oxide layer after 200 hours at $150^{o}C$. Quantitative RGA data showed that hydrogen levels had decreased

and water levels had increased during oxide reduction which is consistent with the hydrogen reduction reaction. This test demonstrates that the sequence of hydrogen desorbing from base metal and subsequent oxide reduction will take place at $150^{\circ}C$ burn-in temperature. Studies with gold over nickel plating showed nickel can diffuse through the gold layer and spread over the gold surface forming a thin layer of nickel oxide which is also capable of being reduced by hydrogen.

Kovar samples exposed to high temperature H_2 brazing increased the subsequent desorbed hydrogen content of the metal, whereas, low temperature H_2 annealing reduced the hydrogen content. A hydrogen bake-out process reduced hydrogen desorption below detectable levels and appeared to be very effective in reducing hydrogen levels in the metal.

Electroplated samples showed inconsistent results. The plating process appeared to absorb hydrogen into the metal or the plating itself was a source of hydrogen.

DATA MATRIX OF BASE KOVAR HYDROGEN DESORPTION

DATA IN % H_2 CC/G BY VOLUME

ND = NONE DETECTED; <0.02 % H_2

I. <u>60 MIL STOCK</u>

<u>LOT</u>	<u>TIME</u>	<u>$100^{\circ}C$</u>	<u>$150^{\circ}C$</u>	<u>$200^{\circ}C$</u>	<u>$250^{\circ}C$</u>	<u>$300^{\circ}C$</u>
510	50 HRS	0.94	2.96			
	100	0.43	0.03			
	150	0.22	0.54			
	200	0.39				
510	200 HRS		3.90	2.99	2.74	3.07
	400		0.13			
	600		ND			
	1000		ND			
823	200 HRS		3.59			
	400		0.03			
120	200 HRS		6.48	2.87	2.77	2.62
	400		0.07	0.10	0.13	0.47
	600		ND			
606	200 HRS		3.38			
	400		0.02			
602	200 HRS		3.16			
	400		0.03			

SG529

II. <u>40 MIL STOCK</u>

<u>LOT</u>	<u>TIME</u>	<u>$100^{\circ}C$</u>	<u>$150^{\circ}C$</u>	<u>$200^{\circ}C$</u>	<u>$250^{\circ}C$</u>	<u>$300^{\circ}C$</u>
26828	50 HRS	1.35				
	100	0.18				
	150	ND				
	200	0.13				
26828	200 HRS		3.70	3.62	3.73	4.15
	400		ND	ND	0.07	0.56
	600		ND			0.33
	800		-			0.33
	1000		ND			0.24
26820	200 HRS		1.68	1.43	1.53	1.82
	400		ND	ND	ND	0.32
	600		ND			0.28
	800		-			0.26
	1000		ND			0.25
27347	200 HRS		2.13	1.96	1.89	2.09
	400		ND	ND	0.02	0.65
	600		ND			0.28
	800		-			0.25
	1000		ND			0.20
24196	200 HRS		ND	ND	ND	0.37
	400		ND	ND	ND	0.25
	600		ND			0.23
	800		-			0.27
	1000		ND			0.20
27770	200 HRS		2.10	2.01	1.76	2.10
	400		ND	ND	ND	0.31
	600		ND	ND	ND	0.40
	800		-			0.09
	1000		ND			0.14
801	200 HRS		1.93	0.69	0.72	1.36
	400		ND	0.04	0.06	0.45
905	200 HRS		0.56			
	400		ND			
003	200 HRS		2.69			1.51
	400		ND			

III. 10 MIL STOCK

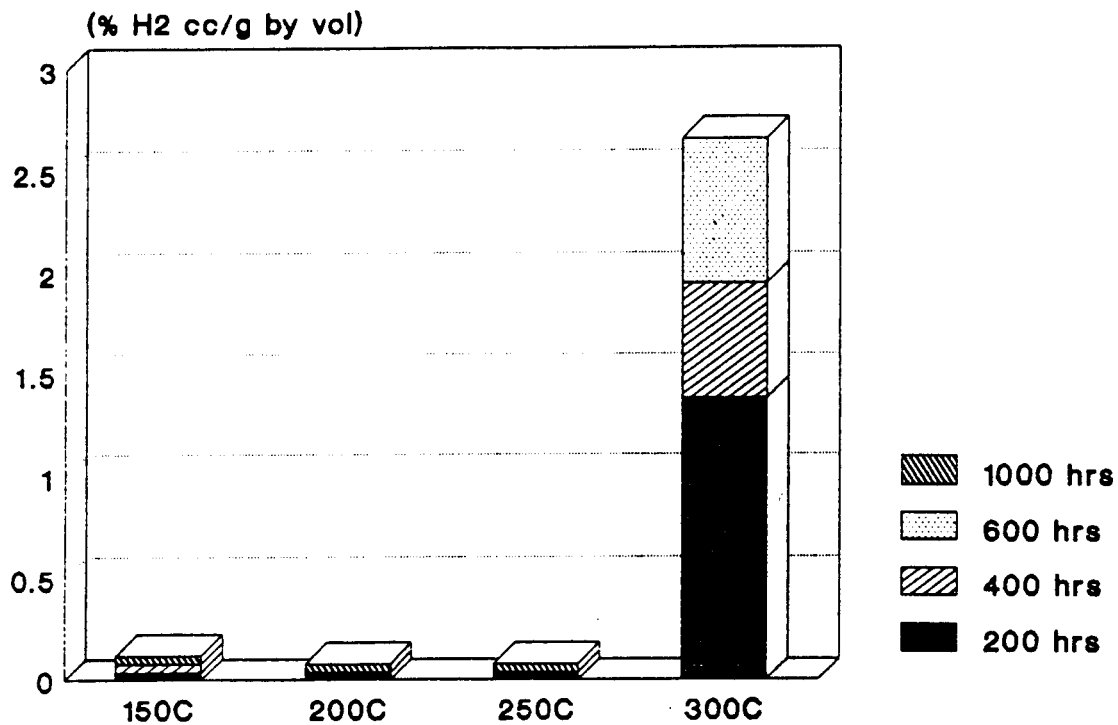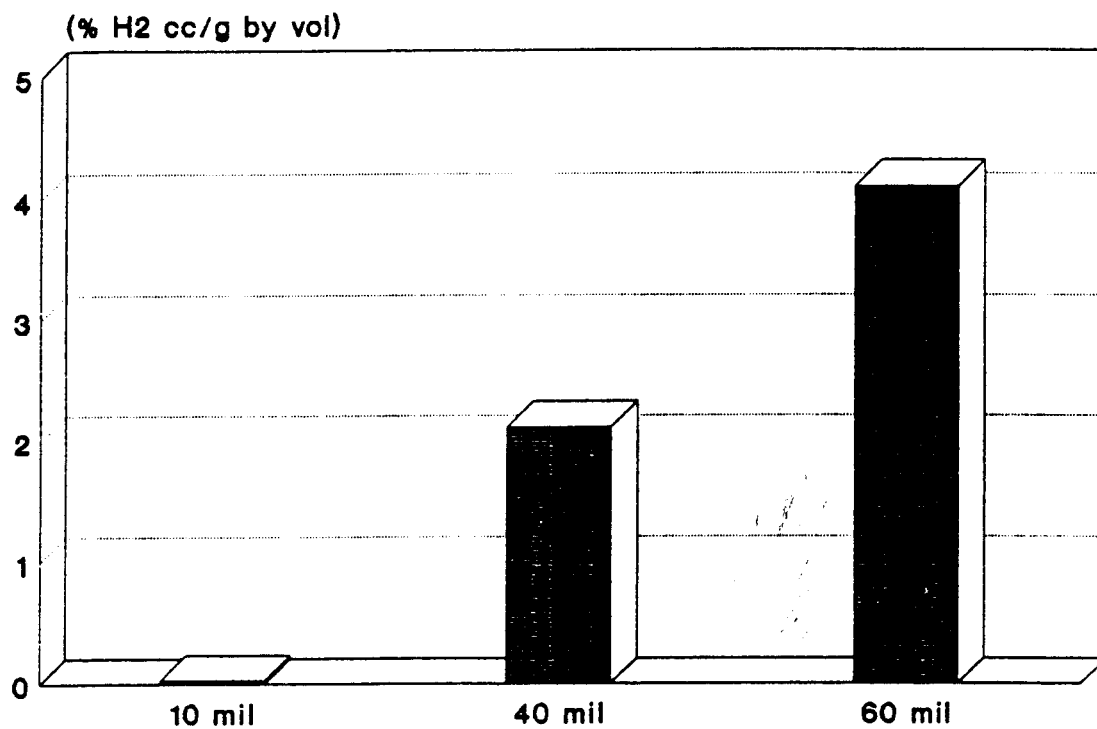| LOT	TIME	$100^{\circ}C$	$150^{\circ}C$	$200^{\circ}C$	$250^{\circ}C$	$300^{\circ}C$
334	200 HRS		ND			1.75
460	200 HRS		ND			0.87
860	200 HRS		ND			1.74
144	200 HRS		ND	ND	ND	1.72
	400		ND	-	-	0.57
	600		-	-	-	0.71
	800		-	-	-	
	1000		ND	ND	0.08	
259	200 HRS		ND			1.05
679	200 HRS		ND			1.17

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TIME/TEMP HYDROGEN DESORPTION
60 mil Kovar Stock
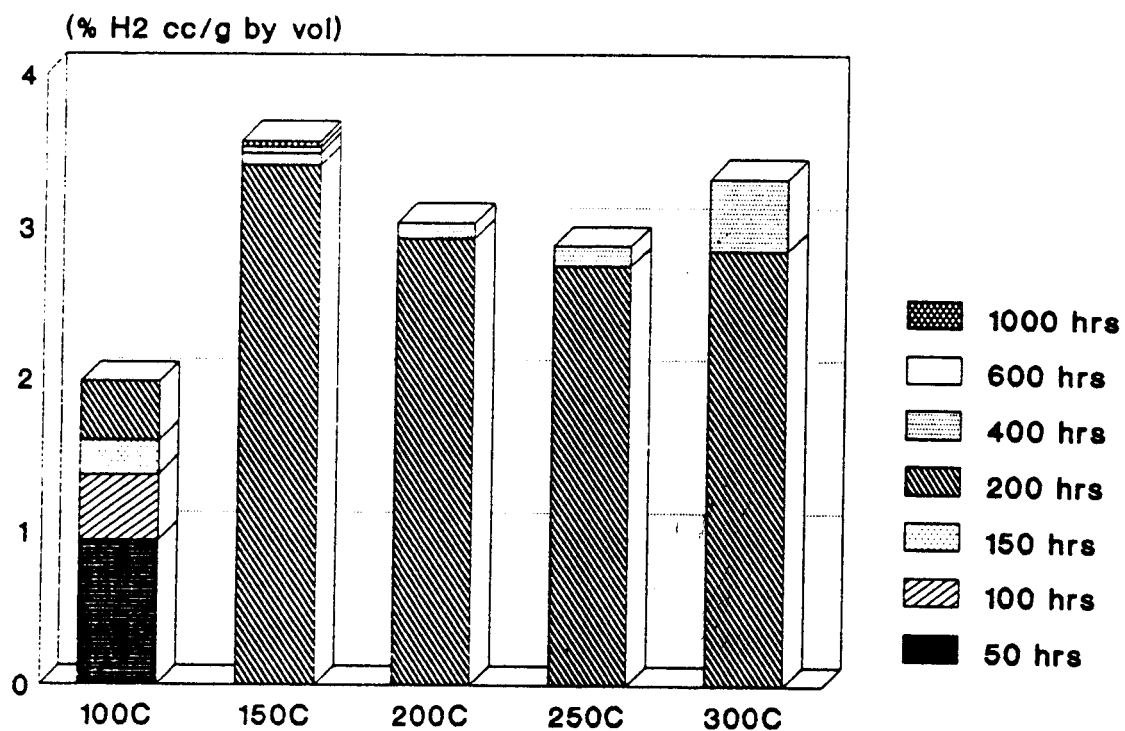
TIME/TEMP HYDROGEN DESORPTION
40 mil Kovar Stock

(% H2 cc/g by vol)

Legend:
- 1000 hrs
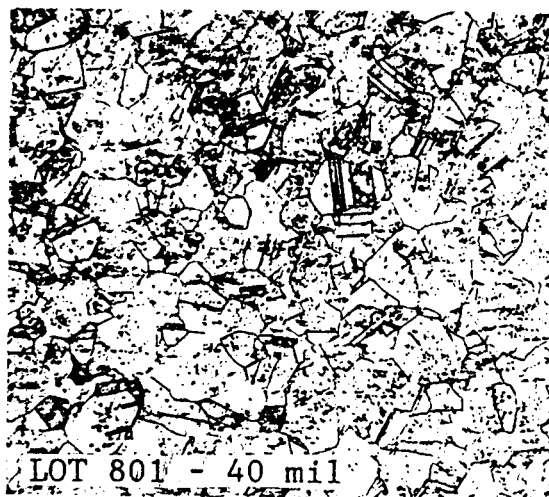- 800 hrs
- 600 hrs
- 400 hrs
- 200 hrs
- 150 hrs
- 100 hrs
- 50 hrs

X-axis: 100C, 150C, 200C, 250C, 300C
Y-axis: 0, 1, 2, 3, 4
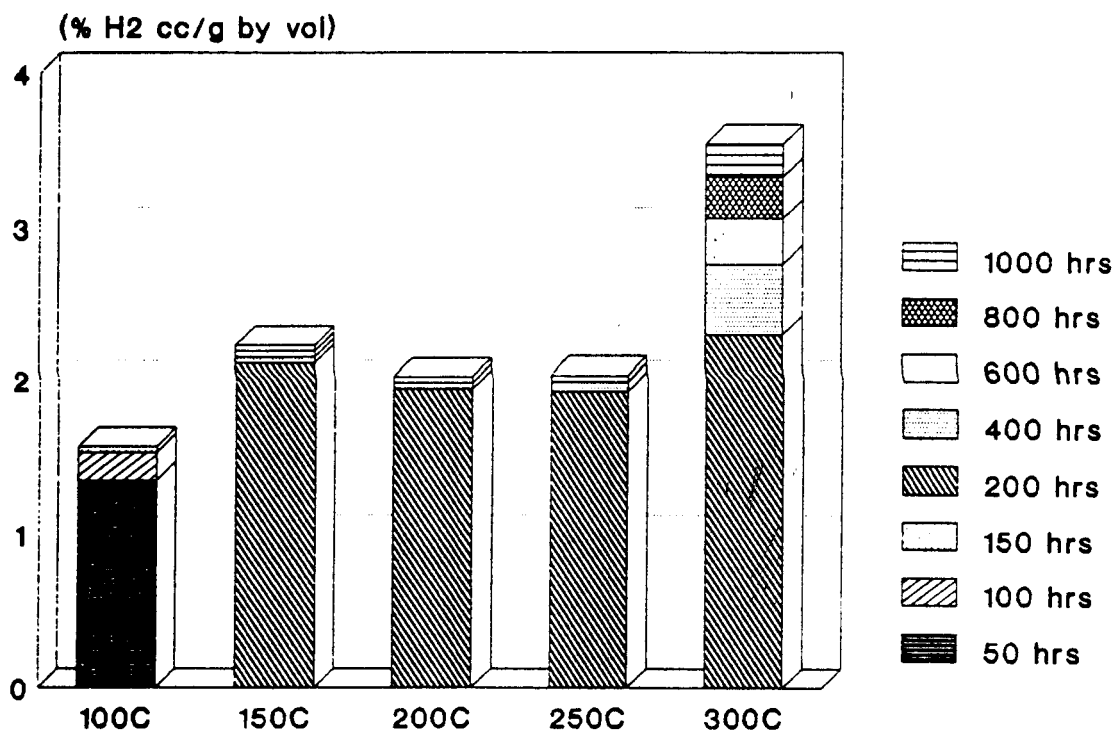
TIME/TEMP HYDROGEN DESORPTION
10 mil Kovar Stock

(% H2 cc/g by vol)

Legend:
- 1000 hrs
- 600 hrs
- 400 hrs
- 200 hrs

X-axis: 150C, 200C, 250C, 300C

Y-axis: 0, 0.5, 1, 1.5, 2, 2.5, 3

COUPON THICKNESS
150C/200HR

(% H2 cc/g by vol)

KOVAR MICROSTRUCTURES, 320x

LOT 144 - 10 mil

LOT 801 - 40 mil

LOT 120 - 60 mil

LOT 26828 - 40 mil
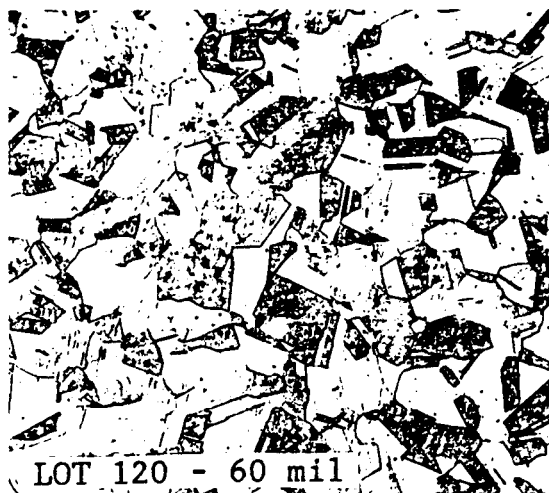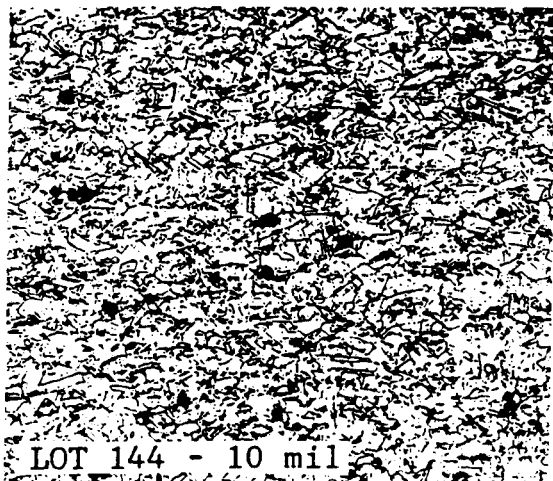
Cu OXIDE REDUCTION STUDY
by Kovar Hydrogen Outgassing

(Thousand ppm)
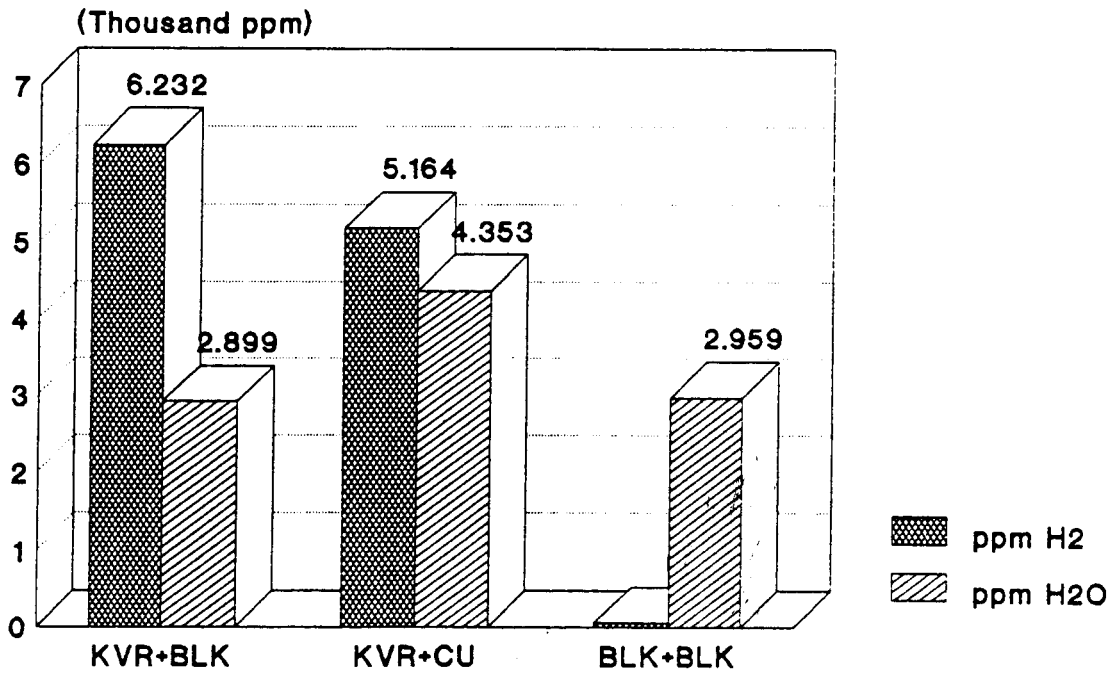
KVR • Kovar Coupon
BLK • Blank Coupon
CU • Oxidized Cu Coupon
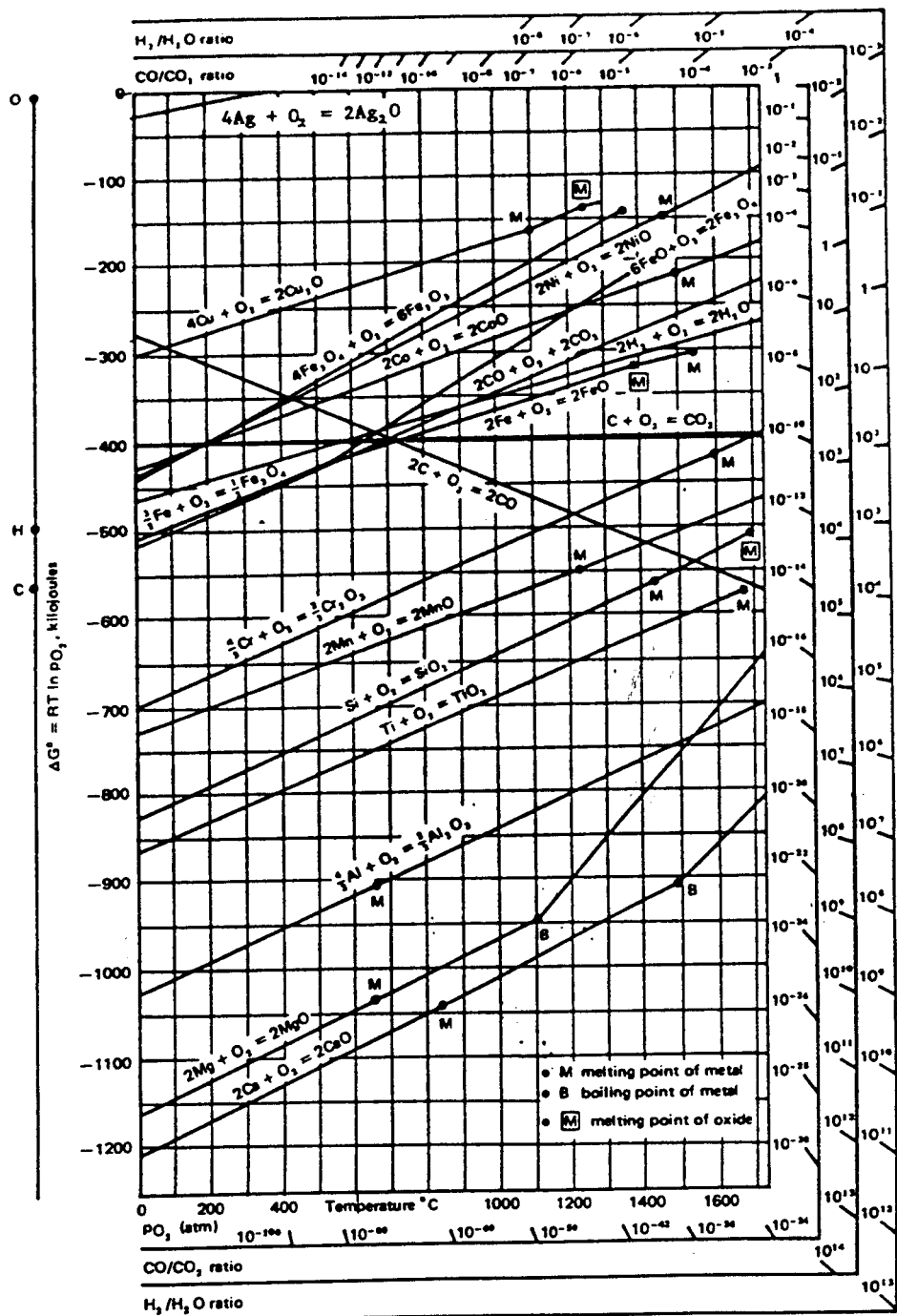
The Ellingham diagram for metallurgically important oxides.

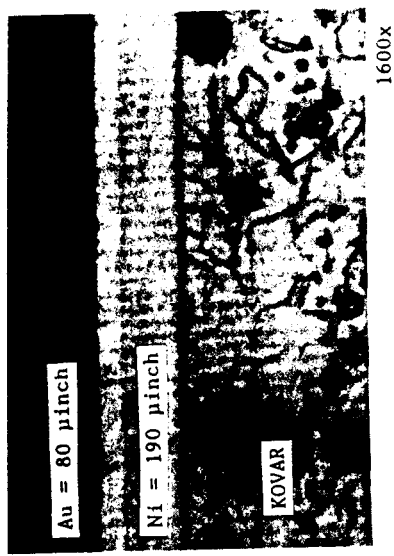Gaskell, D.R. "Introduction to Metallurgical Thermodynamics" Hemisphere Publishing, NY 1981 2nd Edition.

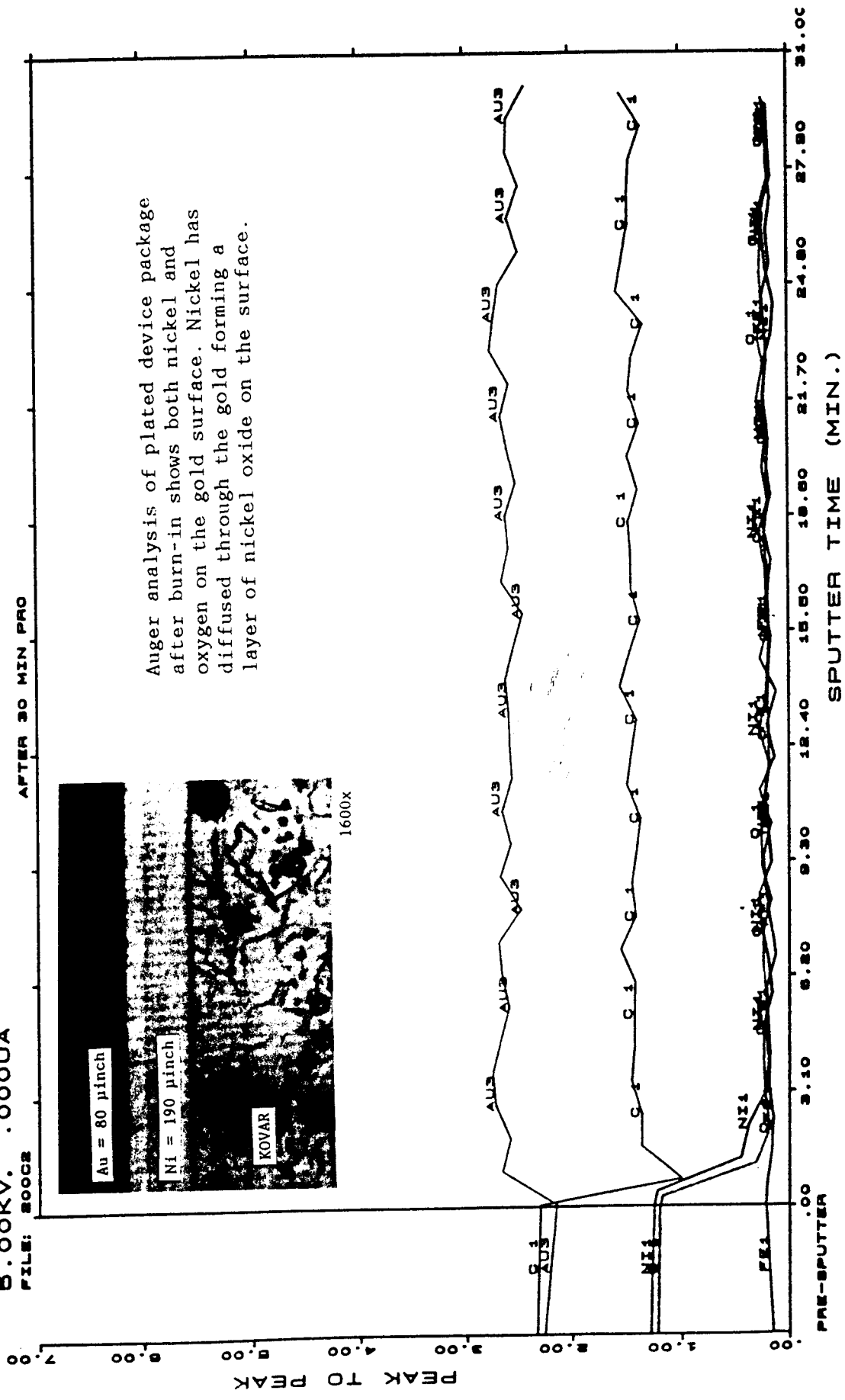AES   PROFILE   XR= 1.5, YR= 1.5   07/26/91
                                  GND= 450   5.0KV, 2.500MA

5.00KV, .000UA   AFTER 30 MIN PRO
FILE: 200C2

Au = 80 µinch

Ni = 190 µinch

KOVAR   1600x

Auger analysis of plated device package
after burn-in shows both nickel and
oxygen on the gold surface. Nickel has
diffused through the gold forming a
layer of nickel oxide on the surface.

PEAK TO PEAK

SPUTTER TIME (MIN.)

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DATA MATRIX OF PREPARED KOVAR COUPONS
HYDROGEN DESORPTION AT 150°C

DATA IN % H_2 CC/G BY VOLUME

ND = NONE DETECTED; <0.02% H_2

		KOVAR COUPON LOTS			
		60 MIL		40 MIL	10 MIL
CONDITION	HOURS	510	120	905	144
VIRGIN STOCK	0	2.12	1.64	0.56	ND
HYDROGEN BRAZE	200	2.61	2.65	1.71	ND
	400	0.04	-	-	ND
HYDROGEN ANNEAL	200	0.76	0.74	0.65	ND
	400	-	ND	-	ND
WET H_2 GLASS SEAL	200	0.25	0.26	0.20	ND
HYDRODEN BAKE OUT	200	ND	ND	ND	ND
	400	ND	ND	-	-
SUPPLIER A Au/Ni PLATE	200	0.06	ND	ND	ND
	400	0.03	0.07	-	0.09
	600	0.09	-	-	-
SUPPLIER B Au/Ni PLATE	200	0.06	0.07	ND	ND
	400	0.13	0.29	-	ND
	600	-	0.16	-	-
SUPPLIER A PROCESS	200	ND	ND	-	0.22
SUPPLIER B PROCESS	200	ND	0.02	-	0.21
H_2 FREE STOCK	0	ND	ND	-	ND
SUPPLIER A PROCESS	200	0.04	ND	-	-
SUPPLIER B PROCESS	200	0.10	0.05	-	-

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Benjamin A. Moore and Joseph A. Carpenter, Jr.