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Kapton HN Investigations

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Contents

Abstract

Kapton HN properties and the properties of the slip additive calcium phosphate dibasic ($CaHPO_4$) were investigated. Impurity analyses were performed on the compound by inductively coupled plasma (ICP) and ion chromatography (IC). Other analyses on the slip additive included: processing solution - dissolution analysis, high-explosive compatibility studies, scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), and particle size distribution. Testing and analyses were also performed on Kapton HN film and other polyimide films that could serve as possible replacements for Kapton HN. The polyimide films that were tested are: Upilex-R, Upilex-S, Upilex-SGA, and Apical. The analyses performed were: infrared (IR), x-ray photoelectron spectroscopy (XPS), SEM/EDS, high-potential breakdown testing, (PVD) physical vapor deposition adhesion tests, and peel tests. Upilex-S flyer cables were also fabricated and successfully test fired.

In addition to these raw material tests, production cables were chemically treated and destructively (high potential) tested. A long-term aging environment for production cables was also selected, and aging tests were begun.

Introduction

Early in the 1980s, DuPont introduced a "new" Kapton that was designated Kapton HN. Kapton H was already being used extensively in Mound's flexible cables, and soon after its introduction, we began receiving the new Kapton HN. By 1987, Kapton H was only being made by DuPont as a special order item.

Kapton HN is Kapton H, but with a slip additive added. Analyses at Mound showed that the additive was calcium phosphate dibasic ($CaHPO_4$). SEM (Scanning electron microscopy) has shown that some of the slip additive particles are large (≈80% of the thickness of the polyimide film), some protrude from the surface of the film, and some are cracked.* Work at SNLA

*Acton, A. E., "Kapton H versus Kapton HN Film for Flexible Circuits," a report to W. B. Vandermolen, 30 September 1987.

and Mound has shown that chemical processing with 10% KOH can dissolve the Kapton polyimide and cause some of these particles to fall out of the film leaving pits in the surface. These observations caused concern over the electrical and mechanical integrity of the film and the long-term reliability of products made with Kapton HN.

Experimental

This section is divided into three subsections. First, work performed on the slip additive in Kapton HN is presented, then work performed on polyimide films, and, last, work with fully fabricated components.

Slip Additive

As mentioned in the Introduction, the slip additive in Kapton HN is calcium phosphate dibasic ($CaHPO_4$). The identity of this compound was determined by P. S. Wang and others at Mound early in 1987. Calcium phosphate dibasic is soluble in acids, slightly soluble in water, and somewhat less soluble in more basic solutions. SEM of the powder (Figure 1) shows that it

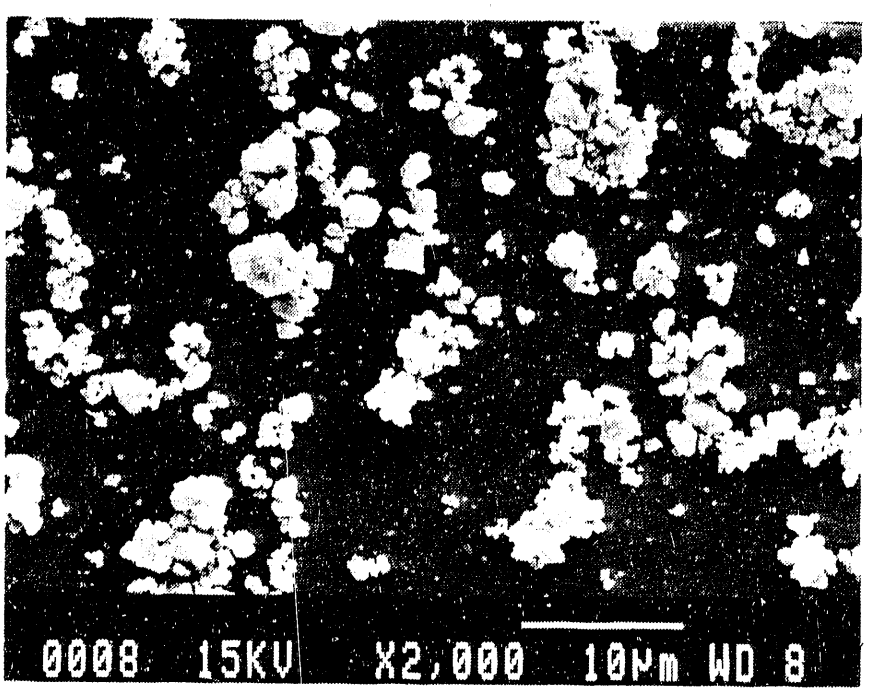

Figure 1 - Scanning electron micrograph of $CaHPO_4$ showing the powder's tendency to form agglomerates.

forms agglomerates from smaller particles. First attempts at preparing SEM samples were unsuccessful because of the tendency of the slip additive to agglomerate. The SEM sample shown in Figure 1 was made by ultrasonically treating a small amount of the additive in ethanol, then wicking some of that mixture into an eyedropper and spraying it onto the substrate. EDS (energy dispersive spectroscopy) of the additive showed no major impurities.

The slip additive was also analyzed for impurities by ICP (inductively coupled plasma) and IC (ion chromatography). These results and the vendor specifications are shown in Table 1. No major impurities were found, but the IC detection limit for fluoride is 400 ppm and the vendor would accept as much as 2500 ppm choride. This sample, however was much lower in choride.

Manufacture of flexible cables at Mound involves passing the cable through various solutions to clean, etch, develop, and plate circuits. The extent of solubility of calcium phosphate dibasic ($CaHPO_4$) in these solutions was determined by detecting the concentration of calcium by ICP; Table 2 shows

Table 1 - $CaHPO_4$ IMPURITIES

	Vendor Specifications	Mound Analyses (ppm)
Chloride	0.25% Max (2500 ppm)	46 (IC)[a]
Fluoride	50 ppm Max	0 (IC)[b]
Sulfate	0.5% Max (5000 ppm)	-
Arsenic	3 ppm Max	
Heavy Metals	30 ppm Max	
Lead	5 ppm Max	0 (ICP)[c]
Acid Insolubles	0.2% Max (2000 ppm)	
		Fe 200 (ICP)
		Mg 500 (ICP)
		Mn 50 (ICP)
		Na 50 (ICP)
		Si 300 (ICP)
		Sr 200 (ICP)
		Cr < 20 (ICP)
		B < 20 (ICP)

[a]IC = ion chromatography.

[b]Note the IC detection limit for fluoride is 400 ppm.

[c]ICP = inductively coupled plasma.

Table 2 - MOUND PROCESSING SOLUTIONS WERE CONTACTED WITH $CaHPO_4$ TO DETERMINE SOLUBILITY

	Ca Before (μg/mL)	Ca After (μg/mL)
Reverse Osmosis Water	0	53
Stripper 5% KOH	0	<2
Developer Na_2CO_3	0	10
Plating 15% H_2SO_4	0	875
Diff. Bond 50% HCl	0	27,787
200 Proof C_2H_5OH	0	<2
Etchant $FeCl_3$	58	26,401
Plating $Ni(SO_3NH_2)_2$	0	584

the results. In general, the more acidic the solution the more slip additive it could dissolve. The concentration (μg/mL) of $CaHPO_4$ can be back calculated by dividing the μg/mL of Ca by 0.29. Also, this test was performed by putting 10 g of slip additive in 100 mL of each solution; so if all the slip additive were dissolved, the maximum concentration would be 0.1 g/mL of $CaHPO_4$.

Since most Kapton film used in cables at Mound is thin (either 1 or 2 mils), the particle size distribution of the $CaHPO_4$ is important. DuPont claims no particles larger than 7 μm diameter go into their films, but one 40 μm particle was observed in a 2 mil (50 μm) film.* The particle size distribution was determined by using a Coulter Counter. The distribution is shown graphically in Figure 2. Most of the particles are from 1 to 5 μm in diameter. However, 4% of the particles are 10 to 20 μm in diameter, and none larger than 20 μm were found in this sample.

In some applications, Kapton HN is in direct contact with high explosives in detonators. Because of this contact and because the slip additive is exposed at the surface of the film, high-explosive compatibility tests were performed with $CaHPO_4$. The explosives tested were HNS (hexanitrostilbene), TATB (triaminotrinitrobenzene), HMX (cyclotetramethylene tetranitramine), and

*Acton, A. E., "Kapton H versus Kapton HN Film for Flexible Circuits," a report to W. B. Vandermolen, 30 September 1987.

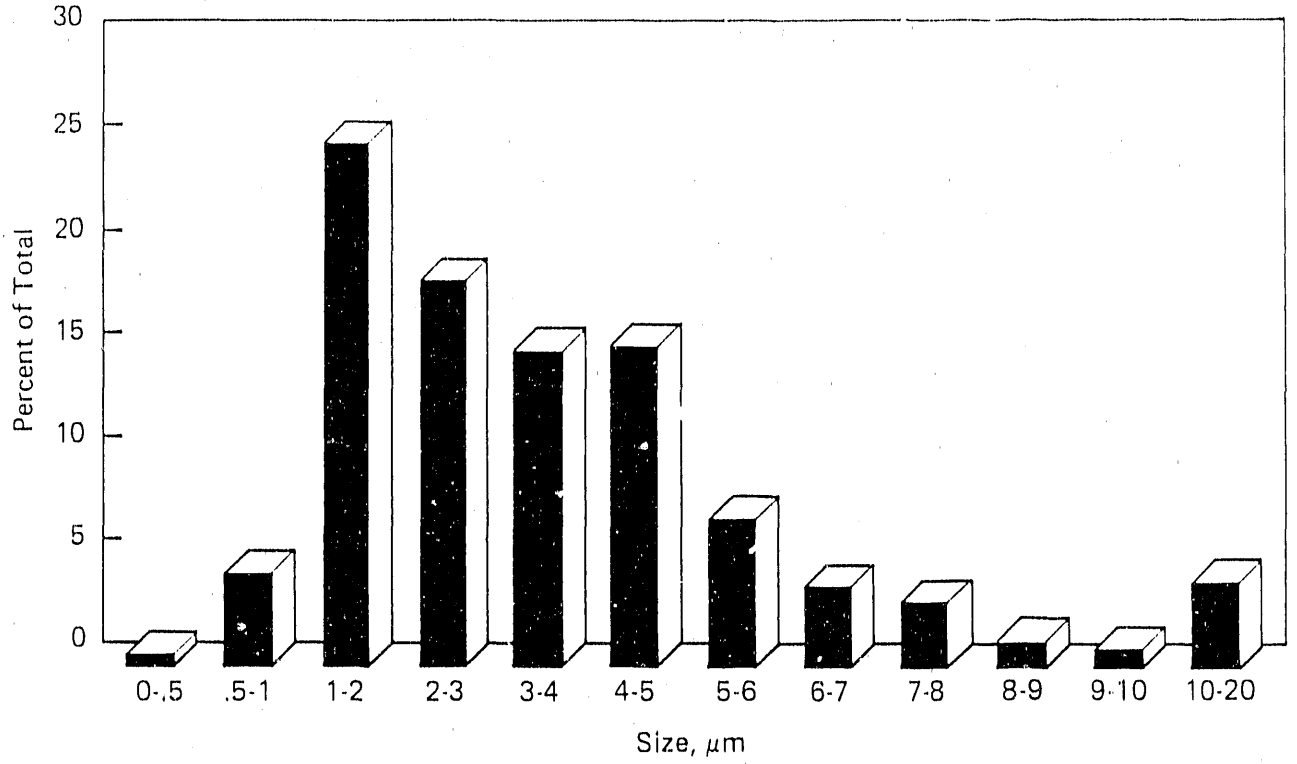

Figure 2 - The particle size distribution of $CaHPO_4$ as determined by Coulter Counter analysis.

LX-16 [PETN (pentaerythritol tetranitrate) with a binder]. HNS, TATB, and HMX were compatible with the $CaHPO_4$. LX-16 showed some reactivity with $CaHPO_4$ at 120 and 100°C. This test was performed using a 50/50 mixture of the slip additive and the high explosive. Since a mixture of this nature is very unlikely to ever occur in a component, a test using actual Kapton HN and LX-16 was conducted. The results of that test showed that LX-16 is compatible with Kapton HN.

Testing of Polyimide Films

This subsection covers the testing of the following polyimide films: Kapton HN, Kapton H, Apical, Upilex-S, Upilex-R, Upilex-SGA.

Infrared (IR) spectra, which were determined for Upilex-S, Kapton H, Apical, Upilex-R, and Upilex-SGA (Figures 3-7), showed that Upilex-S and Upilex-SGA have essentially identical structures. Apical and Kapton H also showed only minor structural differences, whereas structural differences between Upilex-S/Upilex-SGA and Apical/Kapton H were very evident. Upilex-R was

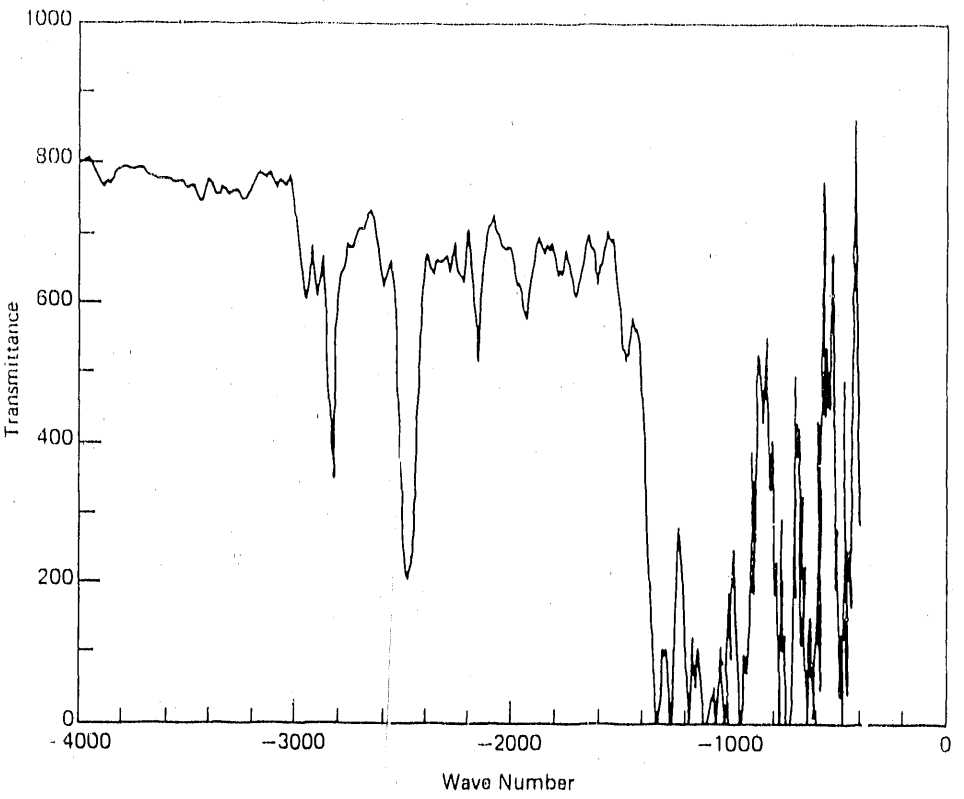

Figure 3 - IR spectral determination for Upilex-S.

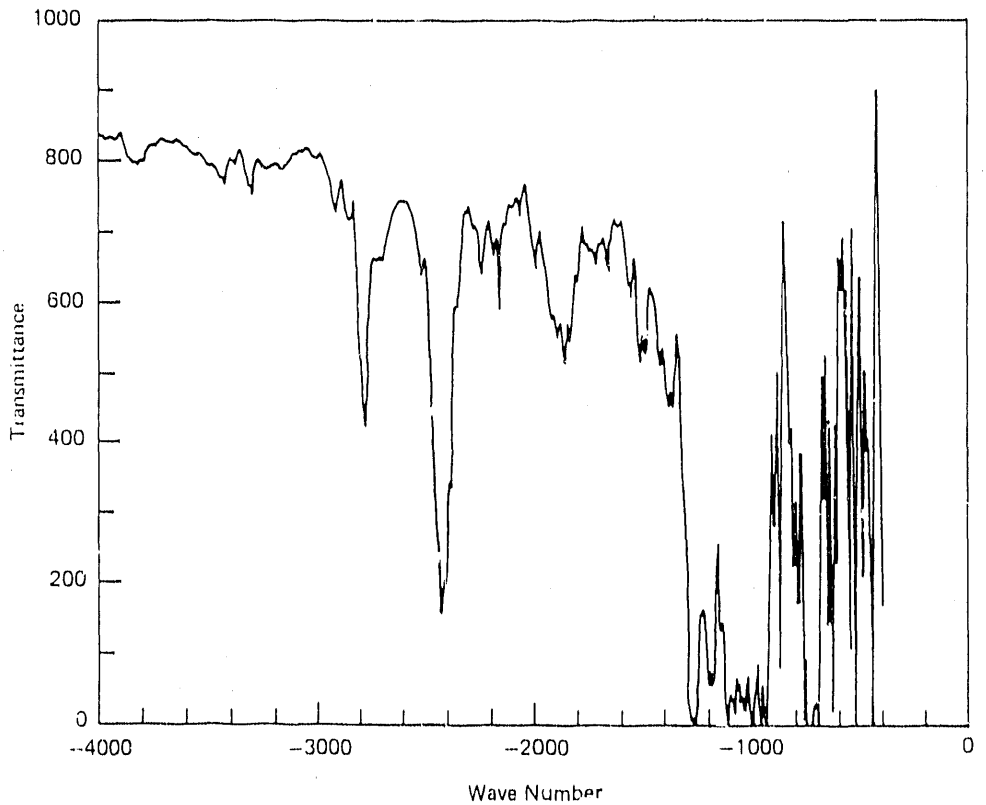

Figure 4 - IR spectral determination for Kapton H.

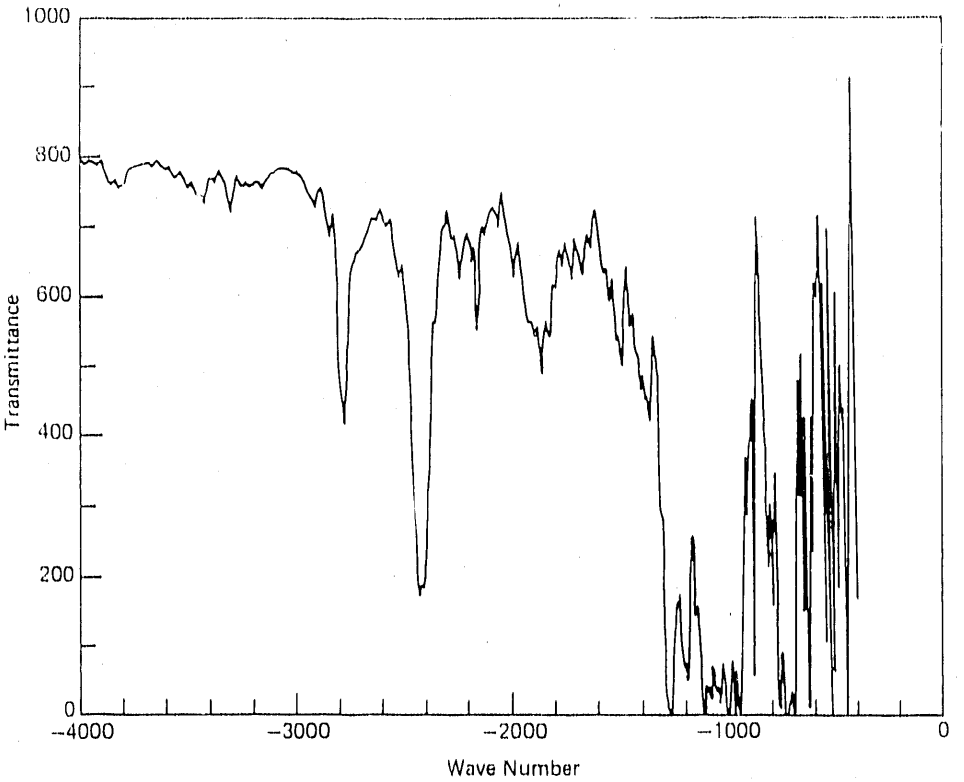

Figure 5 - IR spectral determination for Apical.

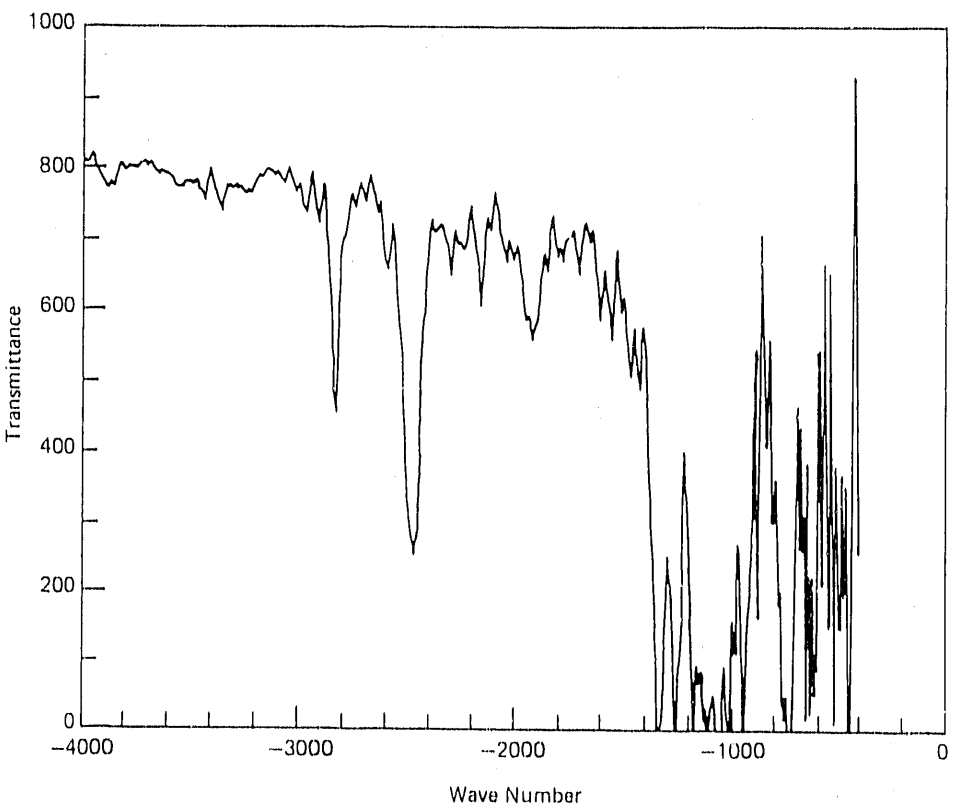

Figure 6 - IR spectral determination for Upilex-R.

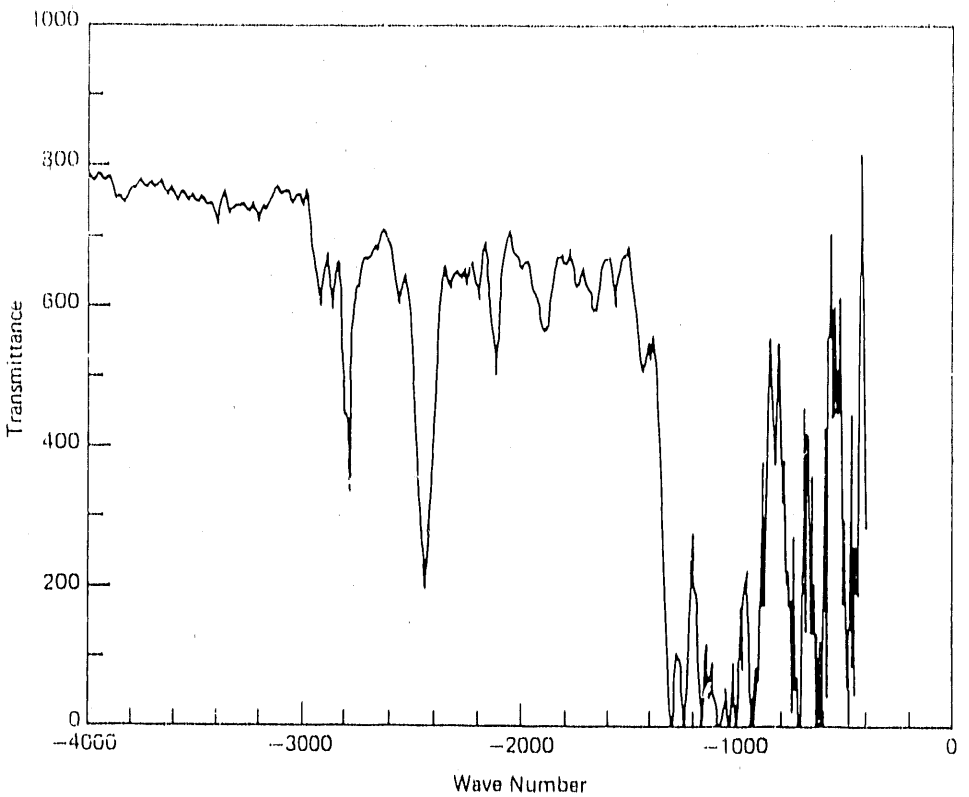

Figure 7 - IR spectral determination for Upilex-SGA.

different from all the other polyimides, showing some similarities to both Upilex-S and Kapton H. IR spectra were not determined for Kapton HN since the main difference between Kapton H and Kapton HN is the prescence of $CaHPO_4$ (the slip additive) in Kapton HN. XPS (x-ray photoelectron spectroscopy) determinations were made on the same polyimides to determine if one side of the Upilex-SGA was coated with something to enhance bordability. No coating on Upilex-SGA was positively detected. The differences from inside to outside of the Upilex-SGA film, with or without cleaning, were no greater than other films that were known to be uncoated. Silicon, however, was detected on the Upilex-SGA. The silicon was present on both sides of the film and could be partially removed with acetone. Silicon was also detected on Upilex-S/Upilex-SGA by SEM/EDS and is believed to be a surface contaminant, possibly from a release agent. The percentages of carbon, oxygen, nitrogen, and silicon, detected by XPS, are given in Table 3.

The Kapton and Upilex films were tested for high-voltage breakdown using 1-in. diameter brass contacts in Fluoroinert.* These tests were conducted to

*A series of perfluorinated liquids used for cleaning electronic components after testing.

Table 3 - ELEMENTAL CONSTITUENTS[a] OF POLYIMIDE FILMS AS DETERMINED BY XPS

Sample		C		O	N	Si
		C=O	C-H			
Kapton H	outside	7.8	76.7	13.4	2.4	---
	inside	10.5	70.0	15.2	4.4	---
	outside, acetone wipe	12.3	62.2	18.8	6.6	---
	inside, acetone wipe	11.9	62.6	19.0	6.5	---
Upilex-R	outside	9.8	72.5	13.9	3.9	---
	inside	9.9	69.0	15.6	5.4	---
	outside, acetone wipe	11.2	67.4	15.8	5.5	---
	inside, acetone wipe	11.2	67.2	16.0	5.6	---
Upilex-SGA	outside	11.7	64.0	17.9	4.9	1.5
	inside	11.4	59.6	20.7	6.1	2.1
	outside, acetone wipe	12.1	61.8	18.7	6.4	0.96
	inside, acetone wipe	13.4	62.1	17.1	6.7	0.73
Upilex-S	outside	13.6	64.0	16.3	5.8	<0.4
	inside	13.3	65.1	14.7	6.9	---
	outside, acetone wipe	12.4	64.4	15.7	7.1	<0.3
	inside, acetone wipe	12.1	65.1	15.4	7.5	---
Apical	outside	11.6	63.4	19.0	6.0	---
	inside	13.8	58.6	20.9	6.6	---
	outside, acetone wipe	12.1	61.7	19.3	6.9	---
	inside, acetone wipe	12.2	61.5	19.1	7.2	---

[a]By percent.

determine the ability of the film to act as an insulator, one of its primary functions in Mound flexible cables. As shown below, Kapton H, Kapton HN, and Upilex-R had average breakdown voltage values in the 20-22 kV range, whereas Upilex-S and Upilex-SGA had average breakdown voltage values in the 16-17 kV range.

Kapton H = 21.51 ± 2.02 kV
Kapton HN = 20.61 ± 7.67 kV
Upilex-R = 21.42 ± 0.16 kV
Upilex-S = 16.48 ± 1.07 kV
Upilex-SGA = 16.44 ± 0.87 kV

The confidence limits on the mean values were calculated at the 95% confidence limit using the formula: mean ± $ts/\sqrt{n}$, where t is the student t, s is the standard deviation, and n is the number of samples. The actual values that were obtained are given in Table 4.

Table 4 - HIGH-POTENTIAL BREAKDOWN TEST RESULTS ON TWO-MIL FILMS IN FLUORINERT[a]

Kapton HN	Kapton H	Upilex-R	Upilex-S	Upilex-SGA
21.21	19.84	21.73	17.90	16.57
22.43	24.01	21.47	17.05	15.54
20.89	17.98	21.38	16.18	17.70
		21.44	16.19	14.93
		21.45	15.36	16.66
		21.14	17.79	17.19
		21.34	14.89	16.49

[a]Results are expressed in kV.

For the bridges in Mound cables, the adhesion of a thin metal coating to the film is very important. To compare the adhesion strengths of a thin metal film to each of these polyimides, actual bridges are made by PVD (physical vapor deposition). A plasma cleaning step is used at the beginning of the metal deposition process. Half of each bridge has a stud glued to the metal coat, and a ceramic disk (aligned with the stud above) glued to the underside of the film (Figure 8). The assembly is then pulled apart in a test machine, and the force is measured; the failure mode is also noted. Some parts fail more than one way, but the first failure is the significant one. Table 5 shows the average strength at failure, the confidence limits, and the failure mode. In referring to Table 5 and Figure 8, the substrate is the polyimide film, ADH indicates a failure in the epoxy adhesive between the stud and the bridge, AS indicates a failure in adhesion of the metal to the polyimide, IS indicates a failure in the polyimide substrate, and SW indicates a failure of the Scotchweld adhesive. From Table 5, it can be clearly seen that the Upilex polyimides had the greater adhesion strengths with the metal film; this could be related to their greater modulus values.

The fact that Kapton HN had more failures in the substrate than any other film was also noteworthy.

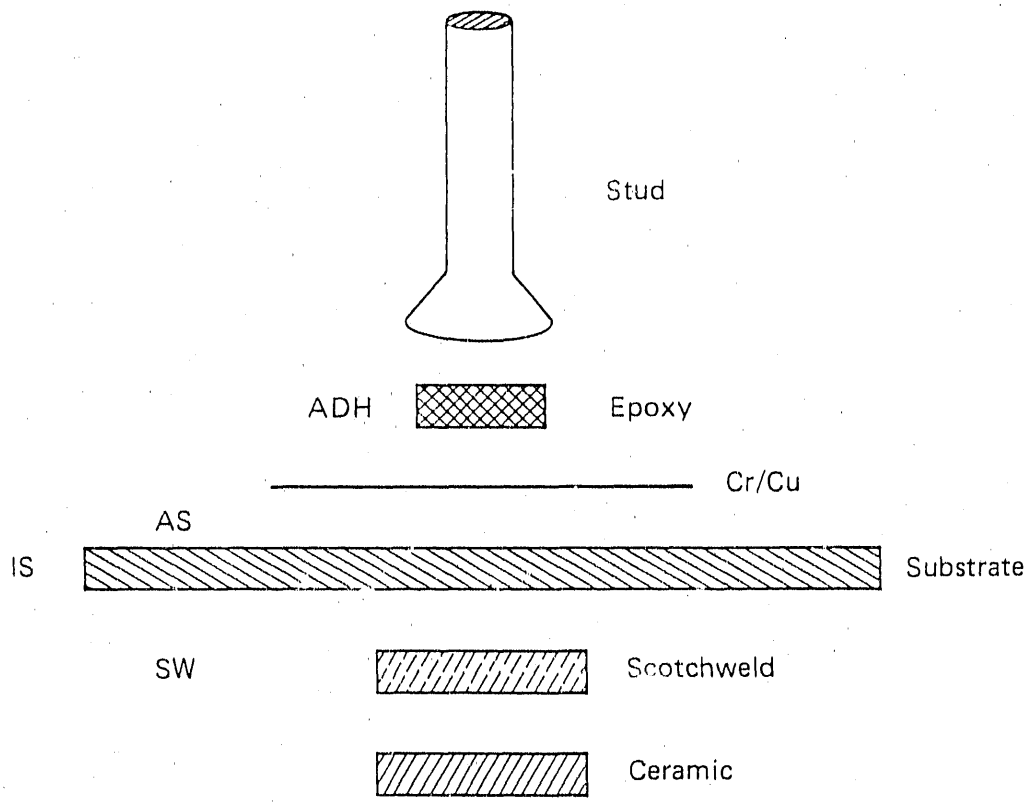

Figure 8 - Exploded view of half a bridge showing: stud glued to metal coat, and ceramic disk (aligned with the stud above) glued to the underside of the substrate (polyimide film). The potential failure modes (ADH, AS, IS, and SW) are also shown.

Table 5 - PVD BUTT TENSILE TEST RESULTS

Material	Rupture Strength at Failure (psi) $\bar{x} \pm ts/\sqrt{n}$ 9 df	First Failure Mode				
		ADH	AS	IS	SW	NF
Kapton H	5.43 ± 0.89	4	3	1	2	0
Kapton HN	5.77 ± 0.32	3	0	5	2	0
Upilex-S	8.67 ± 0.55	5	3	0	1	1
Upilex-R	7.53 ± 0.86	10	0	0	0	0
Upilex-SGA	8.76 ± 0.74	10	0	0	0	0
Apical	5.75 ± 0.40	9	0	0	1	0

Peel tests were performed on all of the polyimide films under study. The results are tabulated in Table 6. All of the results were much lower than expected. Past peel tests with Kapton H and Kapton HN averaged around 7 lb/linear in. Since all the samples yielded lower than expected results, this work will be repeated.

Besides being used as an insulating medium, polyimide films (Kapton) are used as flyer material in Mound's flexible cables. Flyer performance of Upilex-S was compared to that of Kapton H by fabricating MAD-1079 cables with Upilex-S flyers. The data summarized in Figure 9 indicate that there is little if any difference between the performance of a Kapton flyer and an Upilex-S flyer.

Testing of Fully Fabricated Components

Some of the cable manufacturing steps involve the use of an etching solution that contains potassium hydroxide (KOH). Since this step, which has been known to dissolve Kapton, causes some of the slip additive ($CaHPO_4$) particles to be released from the surface of the film, concern was expressed about the electrical integrity of the film with pits in its surface. Consequently, five MC3926 cables were exposed to a 10% solution of KOH at 150°F for 2 min. This exposure represents a slightly more intrusive environment than what would be experienced during the course of normal processing. Afterwards, these cables, along with five untreated cables, were high-potential breakdown tested to destruction. The results, which are tabulated in Table 7, show

Table 6 - PEEL STRENGTH TEST RESULTS[a]

Sample No.	1	2	3	4	5	6	7	8
Apical	T[b]	T	2.0	T	T	T	1.5	T
Upilex-R	1.1	1.1	1.3	1.4	1.5	1.3	0.97	1.1
Upilex-SGA	3.5	3.7	2.9	4.1	3.6	3.2	3.0	3.1
Upilex-S	3.2	4.2	T	4.7	2.7	2.8	4.3	4.2
Kapton H	T	T	T	T	T	T	3.4	T
Kapton HN	3.6	2.9	3.3	2.6	2.7	3.0	2.6	2.7

[a]Results are expressed in lb/linear in.

[b]T indicates the sample tore.

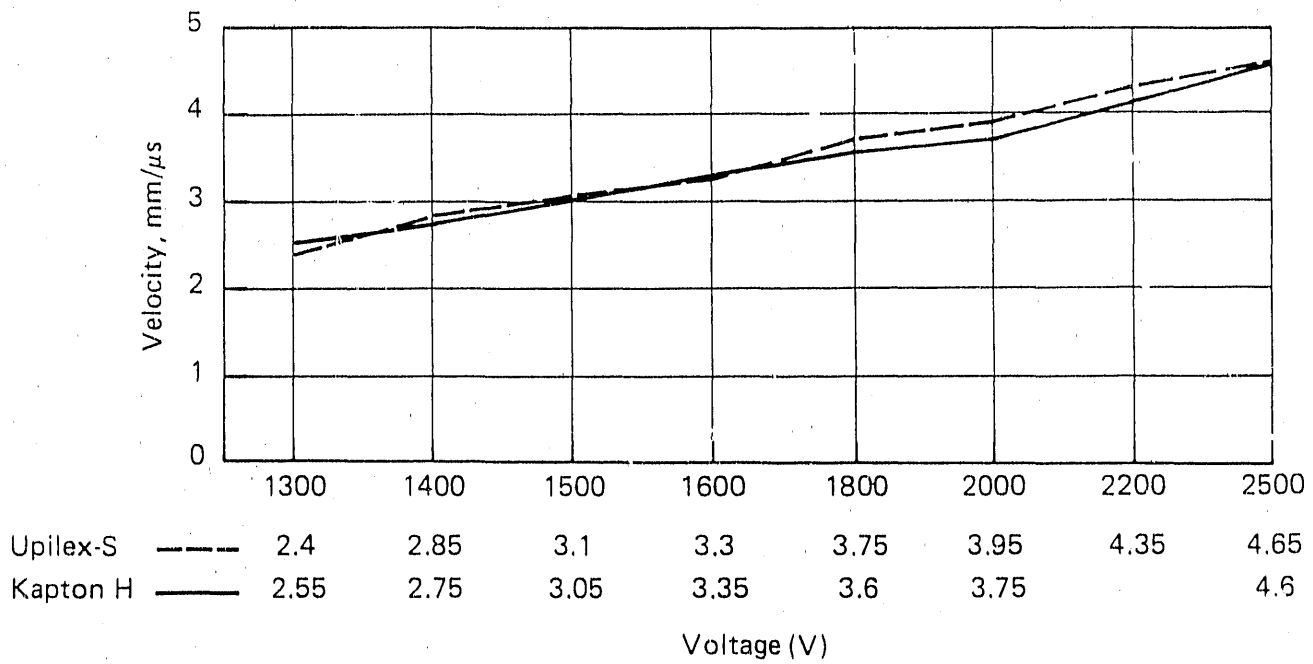

Figure 9 - VISAR results show that there is little difference in performance between Upilex-S and Kapton H flyers.

Table 7 - HIGH POTENTIAL BREAKDOWN TEST RESULTS

	Serial No.	Voltage (kv)
Untreated	8006	36
	8306	27
	8326	36
	8856	36
	8992	38
Treated[a]	8637	38
	8656	36
	8689	32
	8753	39
	8904	39

[a]Five MC3926 cables were treated with KOH at 150°F for 2 min, followed by a 50% HCl rinse at 78°F before being high potential tested to destruction.

that all of the cables retained excellent insulating properties. The lowest failure was at 27 kV and that was one of the untreated cables.

The final concern is long-term aging, and an aging environment has been selected. The cables will be stored at 52% relative humidity (RH) and ambient temperature for 24 hr and then 92% RH and 40°C for 24 hr. This cycle will be repeated until the cable has been appropriately aged; then, the cable will be visually inspected for such deleterious effects as delamination and discoloration before being high-potential breakdown tested to destruction. These results will then be compared to aged cables that have seen no special environment.

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