Solvent Resistance of Parylenes C,N,D

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ABSTRACT

The effect of a wide variety of organic solvents on parylenes C, N, and D was investigated.

Six classes of organic solvents were examined: alcohol (isopropyl), ketones (acetone and 2,4-pentanedione), aliphatic hydrocarbon (iso-octane), aromatic hydrocarbon (xylene), chlorinated olefin (trichloroethylene), chlorinated aromatics (chlorobenzene and O-dichlorobenzene), heterocyclic base (pyridene), and fluorinated solvent (trichlorotrifluoroethane).

These solvents had a minor swelling effect on the parylenes with a 3% maximum increase in film thickness. The swelling was found to be completely reversible after the solvents were removed by vacuum drying.

Some inorganic reagents were also examined. These included the following: de-ionized water; 10% solutions of sodium hydroxide and ammonium hydroxide; non-oxidizing acids, hydrochloric and sulfuric in concentrated and 10% solutions; and oxidizing acids, nitric and chromic, in concentrated and 10% solutions.

The diluted inorganic reagents had little effect on the parylenes. The acids at 10% concentrations had virtually no effect at room temperature and, except for chromic, no effect at 75°C. Concentrated acids at room temperature (23°C) had little effect. Under severe conditions, 75°C for 90 minutes, all acids had a measurable effect ranging from 0.7% swelling with hydrochloric to 8.2% with chromic. Additionally, nitric acid under these same severe conditions caused severe degradation. Both concentrated nitric and sulfuric acids caused some discoloration.

INTRODUCTION

This Technology Letter attempts to answer the questions, "Are the parylenes themselves resistant to solvents, and do they protect substrates from solvent attack? And if so, to what degree?"

Earlier experience had indicated that parylenes N, C, and D were insoluble in all common solvents. Parylene C, it was found, could be dissolved in high boiling liquids such as l -chloronaphthalene or benzoyl benzoate at temperatures above 150°C. However, these solvents are seldom encountered in the electronics industry. Of greater importance are those solvents and reagents used in processing, especially in cleaning, of components and assemblies. This study was undertaken to quantitatively measure the effect of the more common solvents and reagents on the parylenes. Included also were certain hydrocarbons serving as models for fuels. The organic liquids chosen for this study were selected as being representative of typical solvent classes. The protection provided to the coated substrates by the parylenes was also observed.

It was also known that the parylenes were inert to inorganic reagents (except for oxidizing agents). The work reported here and quantitative results given confirmed this conclusion.

EFFECTS OF ORGANIC SOLVENTS

A. On Parylene Films
B. Films of parylenes N, C, and D, between 0.5-1.5mL in thickness, were deposited and then removed from glass plates. Applying a water soluble release agent to the plates prior to parylene depositions facilitated removal. Film thickness was measured optically by an infrared (IR) technique. Film strips were immersed in the test liquids for 90 minutes at room temperature and the thickness was re-measured by the IR method. In every case, equilibrium (no further thickness change) was reached before 90 minutes. The percent thickness change can either be due to swelling or the solvent

content of the film after surface drying. In no case was there an apparent decrease in the original film thickness.

TABLE I

Swelling Caused by Organic Solvents at Room Temperature

SOLVENT		% SWELLING PARYLENE		
Class	Test Member	N	C	D
Alcohol	Isopropyl	0.3	0.1	0.1
Aliphatic Hydrocarbon	Iso-Octane	0.2	0.4	0.3
Amine	Pyridene	0.2	0.5	0.5
Aromatic Hydrocarbon	Xylene (mixed)	1.4	2.3	1.1
Chlorinated Aliphatic	Trichloroethylene (TCE)	0.5	0.8	0.8
Chlorinated Aromatic	Chlorobenzene	1.1	1.5	1.5
Chlorinated Aromatic	O-Dichlorobenzene	0.2	3.0	1.8
Fluorocarbon	Trichlorotrifluoroethane	0.2	0.2	0.2
Ketone	Acetone	0.3	0.9	0.4
Ketone	2,4-Pentanedione	0.6	1.2	1.4

Slight, but measurable, swelling was detected in each case, the maximum being 3% caused by O-dichlorobenzene on parylene C. (This, incidentally, is a solvent for parylene C removal at its boiling point of 180°C.)
After measurement, immersion in the test solvent, and re-measurement, the test strips were dried overnight under a vacuum at room temperature. The thickness was re-measured by the IR technique. In every case, the thickness returned to the original value.
Additional parylene strips were used for immersions in the organic solvents at elevated temperatures. The temperature chosen was either the boiling point of the solvent or 75°C, whichever was lower. Strips were immersed for 120 minutes. Again, longer immersion time did not cause further dimensional changes. Swelling results are given in Table II.

TABLE II

Swelling Caused by Organic Solvents at Elevated Temperatures

SOLVENT		% SWELLING PARYLENE			
Class	Test Member	Temp(°C)	N	C	D
Alcohol	Isopropyl	75	0.3	0.2	0.1
Aliphatic Hydrocarbon	Iso-Octane	75	0.3	0.5	0.3
Amine	Pyridene	75	0.4	0.7	0.7
Aromatic Hydrocarbon	Xylene (mixed)	75	2.1	3.3	1.9
Chlorinated Aliphatic	Trichloroethylene (TCE)	74	0.7	0.9	0.9
Chlorinated Aromatic	Chlorobenzene	75	1.7	2.0	2.1
Chlorinated Aromatic	O-Dichlorobenzene	75	0.3	1.4	0.8
Fluorocarbon	Trichlorotrifluoroethane	37	0.2	0.3	0.2
Ketone	Acetone	56	0.4	0.9	0.4
Ketone	2,4-Pentanedione	75	0.7	1.8	1.6

As with the tests at room temperature, slight, but measurable, swelling was detected in each case. The maximum swelling of 3.3% was observed with xylene (mixed) on parylene C.

When the parylene test strips were dried overnight in a vacuum, the thickness returned to the original values.

From these data, it is concluded that at temperatures under 75°C, organic solvents have only a slight swelling effect on the parylenes and that this effect is completely reversible. In general, the swelling effect is most pronounced with aromatic liquids, especially chlorinated aromatics. Alcohols, aliphatic hydrocarbons and fluorocarbon solvents have the least effect.

On Parylene Coated Substrates

Test coupons of epoxy G-10, copper, glass, and steel were cleaned and treated for adhesion using standard techniques prior to application of a parylene coating to a thickness of 0.5mL. One substrate of each type was tested to determine the degree of adhesion before immersing the remaining substrates in the test solutions. ASTM D-3002-71, "Evaluation of Coatings for Plastics", was chosen for determining the degree of adhesion.

Specimens are prepared by making eleven parallel cuts, 1/16 inch apart with a razor blade, and a similar set of cuts 90 degrees to the first. 3M #610 tape is then pressed firmly over the crosshatched area, using a ball point pen eraser, leaving one end of the tape free for pulling. The tape is rapidly removed using one continuous pull. The number of removed squares is counted to determine the percent failure or percent loss of adhesion. The control specimens all passed without any squares being removed.

The coated coupons of each substrate type were immersed in the solvents shown in Table I and were removed at intervals of 15, 60, 120, 240, and 360 minutes. After rinsing with distilled water, the specimens were tested using the ASTM method described above.

The results of this evaluation showed that the adhesion of all three parylenes was unaffected by immersion up to six hours at both room and elevated temperatures. The appearance of the underlying substrates were unchanged by the tests, indicating the parylenes are effective barriers to the solvents tested.

EFFECTS OF INORGANIC REAGENTS

A. On Parylene Films

Parylene N, C, and D films removed from glass, as described above, were immersed in the reagents listed in Table III. Thickness, by the IR method, was measured after 90 minutes. Except for with the oxidizing acids, equilibrium (no further thickness change) was reached before the period elapsed. Results are given in the following Table:

TABLE III

Swelling Caused by Inorganic Reagents at Room Temperature

REAGENT		% SWELLING PARYLENE			
Class	Test Member	Concentration	N	C	D
Non-Oxidizing Acid	Hydrochloric	10%	0.0	0.0	0.1
Non-Oxidizing Acid	Hydrochloric	37%	0.2	0.0	0.5
Non-Oxidizing Acid	Sulfuric	10%	0.1	0.3	0.2
Non-Oxidizing Acid	Sulfuric	95-98%	0.2	0.4	0.8
Oxidizing Acid	Nitric	10%	0.1	0.1	0.2
Oxidizing Acid	Nitric	71%	0.2	0.2	0.5
Oxidizing Acid	Chromic	10%	0.1	0.1	0.1
Oxidizing Acid	Chromic	74%	0.3	0.0	0.2

Base	Sodium Hydroxide	10%	0.1	0.0	0.1
Base	Ammonium Hydroxide	10%	0.3	0.2	0.1
Inert	De-Ionized Water	100%	0.0	0.0	0.0

Slight swelling was detectable in most cases. No attempt was made to determine reversibility.

Films were also tested at 75°C for 120 minutes. Results are given in Table IV. Under these elevated temperature conditions, there was a definite increase effect due to concentration. While the dilute solutions caused little swelling (maximum 1.2% by chromic acid on parylene N), the concentrated oxidizing acids caused severe degradation of parylenes N and C, and sulfuric acid caused significant swelling of all three parylenes. The bases caused minor but measurable swelling.

Again, no attempt was made to determine reversibility. However, the effects of the concentrated nitric acid were obviously permanent and some sulfonation by the hot sulfuric acid would be expected.

TABLE IV

Swelling Caused by Inorganic Reagents at 75°C

REAGENT		**% SWELLING PARYLENE**			
Class	Test Member	Concentration	N	C	D
Non-Oxidizing Acid	Hydrochloric	10%	0.0	0.0	0.0
Non-Oxidizing Acid	Hydrochloric	37%	2.3	4.1	0.7
Non-Oxidizing Acid	Sulfuric	10%	0.2	0.2	0.6
Non-Oxidizing Acid	Sulfuric	95-98%	5.3	5.1	7.8
Oxidizing Acid	Nitric	10%	0.2	0.1	0.1
Oxidizing Acid	Nitric	71%	**o**	1.85	4.9
Oxidizing Acid	Chromic	10%	1.2	0.0	0.1
Oxidizing Acid	Chromic	74%	8.2	7.8	4.0
Base	Sodium Hydroxide	10%	0.0	0.5	0.4
Base	Ammonium Hydroxide	10%	0.4	0.4	0.9
Inert	De-Ionized Water	100%	0.0	0.0	0.0

o Became brittle and fell apart
5 Turned light brown