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EFFECTS OF GAS PLASMA ON PRINTED CIRCUIT
BOARD MATERIALS

By L. C. Jackson

Published November 1978

Topical Report

Prepared for the United States Department of Energy
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By L. C. Jackson

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Topical Report
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EFFECTS OF GAS PLASMA ON PRINTED CIRCUIT BOARD MATERIALS

BDX-613-2030 (Rev.), Topical Report, Published November 1978

Prepared by L. C. Jackson

This project was established to define gas plasma process parameters for printed circuit board cleaning without damage to the substrate. Process parameters of gas flow, wattage, and time are defined for both oxygen and argon treatments. The surface activity changes of plastics and printed circuit board materials are described. A preliminary evaluation of the life (surface activity) of these materials after plasma treatment is presented. Swell index, contact angle, and Meseran analysis tests were used to measure process parameters, plasma life, and surface changes.

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CONTENTS

Section	Page
SUMMARY.	6
DISCUSSION	7
SCOPE AND PURPOSE.	7
ACTIVITY	7
<u>Process Variables</u>	7
<u>Surface Changes of Plastics</u>	16
<u>Contaminant Removal</u>	16
<u>Theoretical Concepts</u>	18
ACCOMPLISHMENTS.	29
FUTURE WORK.	32
REFERENCES	34
DISTRIBUTION	35

ILLUSTRATIONS

Figure		Page
1	SEM Photographs of the Laminate Side of a Printed Circuit Board Prior to Plasma Treatment (Polaroid).	9
2	SEM Photographs of the Laminate Side of a Printed Circuit Board After Argon Plasma Treatment (Polaroid).	10
3	SEM Photographs of the Laminate Side of a Printed Circuit Board After Oxygen Plasma Treatment (Polaroid).	12
4	Effects of Argon Plasma Processing on Tinned Copper	17
5	Effects of Oxygen Plasma Processing on Tinned Copper	18
6	Effects of Argon Plasma Processing on Printed Circuit Board Laminate.	19
7	Effects of Oxygen Plasma Processing on Printed Circuit Board Laminate.	20
8	Contact Angle Indications of Surface Activity Life After Argon Plasma Treatment of Plastics.	26
9	Effect of Argon Plasma on Surface Activity of Printed Circuit Board Laminate	28
10	Effect of Argon Plasma on Surface Activity of Printed Circuit Board Tinned Copper.	29
11	Effect of Oxygen Plasma on Surface Activity of Printed Circuit Board Laminate	30
12	Effect of Oxygen Plasma on Surface Activity of Printed Circuit Board Tinned Copper.	31
13	Surface Activity of Printed Circuit Board Laminate After Plasma Treatment	32

TABLES

Number		Page
1	Effect of Oxygen Plasma on Surface Condition of Printed Circuit Board Laminate.	15
2	Swell Index of Various Plastics Before and After Argon Gas Plasma Treatment.	21
3	Changes in Plastic Swell Index After Argon Gas Plasma Treatment.	25
4	Life of Plasma Treated Printed Circuit Board Laminate.	33

SUMMARY

This work describes surface activity changes of several plastics, as well as printed circuit board material, after treatment with argon and oxygen gas plasma. Surface erosion and resin removal of printed circuit board laminate occur readily with oxygen, while argon leaves no visible effect.

The following process parameters were established for optimum surface activity and size of equipment: argon plasma at 30 watts, 100 to 200 cm³/minute gas flow, 10 to 20 minutes for metals and plastics; oxygen plasma at 50 to 200 watts, 100 to 200 cm³/minute gas flow, 10 to 30 minutes for metals only.

Although argon can be used for metal and plastic surfaces, oxygen is not recommended for printed circuit board laminate substrates. Printed circuit boards can survive in argon plasma for an extended period of time under various process conditions, based on visible evidence. Oxygen plasma, however, results in surface erosion and subsequent resin removal which limit its use in plasma cleaning of printed circuit boards.

Contact angle, swell index, and Meseran analyses were employed to differentiate surface changes that occurred after plasma treatment. The extent of surface activity life of plasma treated printed circuit boards was shown to be dependent on whether oxygen or argon gas is used. Additional studies in this area are required. Argon plasma, however, appears to provide a greater surface activity life of printed circuit board materials than oxygen plasma. Contaminant removal requires a more extensive study which is beyond the scope of this project.

Evidence is presented which shows that, within certain parameters of argon and oxygen processing, surface activity is temporary. This indicates that dipole or induced dipole orientation occurs with printed circuit board laminates while electron buildup or alignment occurs with tinned copper.

Optimum ion current density of oxygen plasma for the size of equipment used can be determined by Meseran analysis of tinned copper, as demonstrated with oxygen plasma.

DISCUSSION

SCOPE AND PURPOSE

The purpose of this work is to develop fundamental process information for the application of gas plasma to production parts to achieve surface cleanliness, determine the life of plasma treated printed circuit boards, and evaluate surface changes.

ACTIVITY

Plasma is a condition whereby a gas can be ionized at the atomic level by an electric field to cause it to become reactive with surfaces it contacts. The plasma process causes only surface changes; it does not affect the bulk properties of the material. Plasma treatment of surfaces is confined to a layer of 1 to 10 μm in depth.¹ The principal processes by which the molecular weight of the surface layer is changed by plasma are by scissioning (reduction in length of molecule), branching, and cross-linking. The type of surface change that occurs is dependent on the type of surface and the gas used, such as oxygen (diatomic) or argon (noble).

Gas plasma is currently being used at Bendix to optimize cleanliness levels beyond those which can be obtained with solvent cleaning processes. Improved adhesion has been reported following the use of gas plasma treatment of panels prior to adhesive application.^{2,3,4} Accordingly, this work is directed toward establishing several fundamental parameters of plasma processing and its effect on surfaces for its potential in achieving a high degree of cleanliness and improved adhesion.

Contact angle and adhesion tests have been used in industry as an indication of plasma effects on wettability and improved adhesion,^{5,6} while infrared spectroscopy has been used to show surface changes.^{2,3} This work, however, utilizes a new surface characterization technique based on solubility parameter principles and evaporative rate analysis.

Process Variables

The flow of the gas, the applied wattage, the vacuum level, and the time in the plasma constitute the variables in gas plasma processing. This work was performed using a plasma system with a chamber 152 mm in diameter by about 1 m long (6 by 40 in.).

A series of printed circuit board material panels, epoxy laminate on one side, tinned copper on the other, were processed in argon and in oxygen gas plasmas, varying the wattage, gas flow, and time. Meseran analysis and contact angle measurements were made. Scanning electron microscope (SEM) photographs of the laminate side and of the tinned copper side of the printed circuit board material were made at a 35-degree angle for shadow effects (Figures 1 through 3). Gas flow was varied from 50 to 500 cm³/minute. Wattage for argon was kept at 30 watts, and the time was varied from 10 to 60 minutes for each combination of wattage and gas flow condition. Oxygen wattage was varied from 50 to 500 watts with the accompanying gas flow and time variances. Since argon gas excites so easily, excess wattage was not required.

In all cases of argon treated surfaces (30 watts, 10 to 60 minutes, 50 to 400 cm³/minute gas flow), no visible change occurred in the surface condition of the laminate or tinned copper side of the printed circuit board. There were no indications of resin erosion or material removal (Figures 2 and 3) compared to the untreated circuit board (Figure 1). In contrast, only 10 minutes in oxygen plasma caused erosion of the laminate of the printed circuit board. As wattage or time was increased, resin removal occurred which ultimately exposed the glass fibers of the printed circuit board (Figure 3). Actual laminate delamination occurred when wattages of 400 at 400 cm³/minute gas flow were used. Observations on the oxygen treated printed circuit board laminate are given in Table 1.

Thus, visible evidence shows that printed circuit boards can survive in argon plasma for an extended period of time under various process conditions. Oxygen plasma, however, results in surface erosion and subsequent resin removal which preclude its use in plasma cleaning of printed circuit boards.

In the case of oxygen plasma, excessive gas flow reduced the laminate surface activity, as determined by Meseran analysis. Scanning electron microscope photographs suggest that the exposure of the glass fibers is responsible for this decreased activity. On this basis, oxygen gas flow at 200 cm³/minute may be a maximum acceptable process parameter. This condition of reduced surface activity was not observed with argon.

The printed circuit board materials (tinned copper and epoxy laminate) show greater surface activity after oxygen plasma than after argon treatment. Greater surface activity developed on the epoxy laminate with both gases than occurred on the tinned copper. Extended oxygen plasma treatment, however, decreased the surface activity of both the tinned copper and laminate, based on Meseran analysis.

100X

1000X

Figure 1. SEM Photographs of the Laminate Side of a Printed Circuit Board Prior to Plasma Treatment

100X

1000X

GAS FLOW:
10 MINUTES
30 WATTS
50 cm³/MINUTE

Figure 2. SEM Photographs of the Laminate Side of a Printed Circuit Board After Argon Plasma Treatment

100X

1000X

GAS FLOW:
30 MINUTES
30 WATTS
400 cm³/MINUTE

Figure 2 Continued. SEM Photographs of the Laminate Side of a Printed Circuit Board After Argon Plasma Treatment

100X

1000X

GAS FLOW:
10 MINUTES
50 WATTS
50 cm³/MINUTE

Figure 3. SEM Photographs of the Laminate Side of a Printed Circuit Board After Oxygen Plasma Treatment

100X

1000X

GAS FLOW:
10 MINUTES
200 WATTS
200 cm³/MINUTE

Figure 3 Continued. SEM Photographs of the Laminate Side of a Printed Circuit Board After Oxygen Plasma Treatment

100X

1000X

GAS FLOW:
60 MINUTES
200 WATTS
200 cm³/MINUTE

Figure 3 Continued. SEM Photographs of the Laminate Side of a Printed Circuit Board After Oxygen Plasma Treatment

Table 1. Effect of Oxygen Plasma on Surface Condition of Printed Circuit Board Laminate

Plasma Test Conditions (Wattage and Gas Flow)	Surface Observations for Gas Flow Time Indicated		
	10 Minutes	30 Minutes	60 Minutes
50 W, 50 cm ³	Minor surface cracking.	Slight erosion. Barely visible fiber exposure.	Peak leveling. Visible fiber exposure. Surface crevices.
100 W, 100 cm ³	Slight erosion.	Deep crevices.	Plastic barely covering fibers. Fair fiber exposure. Most plastic removed.
200 W, 200 cm ³	Some fiber exposure. Peak and surface erosion.	Plastic barely covering fibers. Fair fiber exposure. Much plastic removal.	Extensive bare fibers. Plastic removal to first layer of fibers.
400 W, 400 cm ³	Moderate fiber exposure. Peak and surface erosion.	Extensive fiber exposure. Melted plastic nodules. Second level fibers visible.	Extensive bare fiber exposure. Second level fibers visible.
500 W, 500 cm ³	Fair fiber exposure.	Extensive fiber exposure. Second level fibers visible. Melted plastic visible.	Extensive fiber exposure. Second level fibers visible. Melted plastic indicated.

The surface activity, based on Meseran data plotted against plasma time for various argon and oxygen process variables, is given in Figures 4 through 7. In all cases, optimum surface activity was obtained with 50 to 200 cm³/minute flow when oxygen plasma was used. Argon, on the other hand, permits a wide range of gas flow selection without damage to the surface of printed circuit boards (50 to 400 cm³/minute).

Surface Changes of Plastics

Swell Index

Swell index has been used to measure the influence of solvents on plastics.⁷ It also can be used to evaluate surface changes that might occur after gas plasma treatment. Eleven plastics and the printed circuit board material were evaluated with 15 solvents, the latter representing a solubility parameter series of varying polarity and hydrogen bonding. The data are given in Table 2.

If the assumption is made that cross-linking of the molecules at the surface of the plastic has occurred because of the argon treatment (30 minutes, 35 watts, 500 cm³/minute gas flow), solubility in the critical or target solvent should be reduced. If cross-linking has not occurred, if unsaturation or scissioning has developed, solubility should be increased. On this basis, the swell-index data from Table 2 can be summarized into solvency groups (Table 3).

The data suggest that polyvinyl chloride (sleeving) and polysulfide (encapsulant) may have altered surface conditions, such as hardness, after excessive plasma processing. All the other plastics showed little or no change.

Contact Angle

Contact angle measurements have been used to evaluate the wettability of surfaces, and therefore surface activity. Low contact angles indicate increased wettability. Evaluation of the surface activity of eight plastics before and after argon plasma was made by contact angle measurements (Figure 8). With one or two exceptions, plasma treatment of plastics yielded water drop contact angles of less than 20 degrees. The low contact angle created by the plasma treatment was not retained by the plastics for very long. However, the improvement of the plastic surfaces remained for more than ten days.

Contaminant Removal

The ability of oxygen and argon gas plasmas to efficiently remove seven potential production-type contaminants from aluminum panels

Figure 4. Effects of Argon Plasma Processing on Tinned Copper

was determined. The contaminants evaluated were residues from aerosol containers, or from direct contamination. Argon processing involved 50 cm³/minute gas flow, 20 watts for 30 minutes. Oxygen processing was for 30 minutes at 100 cm³/minute gas flow at 50 watts.

Meseran analysis of the surfaces was not made because the contaminants still were visible after the plasma treatment. Since the inception of this project, other work has shown that the plasma effectiveness in contaminant removal is dependent upon the amount (concentration)-present and the process time.⁸ The physical nature of the contamination (liquid, semisolid, or cured), as well as the type of contaminant, also appears to influence removal.

Figure 5. Effects of Oxygen Plasma Processing on Tinned Copper

Contaminant removal by plasma requires a more extensive study to establish suitable effective process parameters to accommodate typical contaminants at varying concentrations that are characteristic of a production area.

Each type of organic contaminant will respond to gas plasma according to the gas used, the process conditions, and the chemical nature of the contaminant. Since contaminants can be cured polymers (photoresist), semisolid (solder flux), or liquids (oils), plasma removal requires varying process times. Oxygen plasma results in surface erosion of printed circuit board laminate at a relatively fast rate. Argon plasma, on the other hand, has no visible effect on the laminate. Organic contaminants would respond in a similar manner. Therefore, process time must be determined for the specific contamination problem involved.

Theoretical Concepts

Surface Activity

There are several theories pertaining to what happens to surfaces upon exposure to gas plasma. Each theory is applicable to the

Figure 6. Effects of Argon Plasma Processing on Printed Circuit Board Laminate

conditions of the test and the surfaces involved. Since the Meseran Surface Analyzer can detect surface changes, a measure of the chemical change or surface activity is possible. Utilizing the three surface energy probes representing different polarity levels (nonpolar, weakly polar, and moderately polar), further definition of the type of surface change is possible. The three radioactive surface energies yield varying values which can characterize each surface. Earlier work has shown that clean printed circuit board surfaces (epoxy laminate and tinned metal) have very low Meseran numbers with all three probes. Ordinarily, the presence of organic contaminants results in large Meseran numbers due to the attraction of the radioactive chemical to the contaminant.⁷

Figure 7. Effects of Oxygen Plasma Processing on Printed Circuit Board Laminate

Meseran analysis of plasma treated surfaces, however, is distinctly different. Energy can be transferred from a plasma to a solid through optical radiation, through neutral particle fluxes, and through ionic particle fluxes. Neutral and ionic particle flux

Text continued on page 25.

Table 2. Swell Index of Various Plastics Before and After Argon Gas Plasma Treatment*

Solvent	Teflon		Polyethylene		Polyvinyl Chloride	
	Before	After	Before	After	Before	After
Weak Hydrogen Bonding						
Heptane	0.03	0.05	1.9	1.6	0.04	0
2-ethylhexylchloride	0.01	-0.01	0.7	1.0	0.13	0
Trichlorotrifluoroethane	0.45	0.85	0.7	0.5	0.02	0
Methylchloroform	0.02	0.06	1.9	1.5	0.5	0.75
Toluene	0.01	0.04	3.7	2.8	9.7	3.3
Trichloroethylene	0.11	0.42	10.4	6.3	40.9	12.7
Perchloroethylene	0.11	0.21	7.3	4.8	0.2	0.1
Methylene Chloride	0.11	0.32	3.2	2.5	D**	D
Vinyltrichloride	0.05	0.03	1.5	1.3	97.9	67.4
Moderate Hydrogen Bonding						
2-ethylhexyl acetate	0.06	0.10	0.7	0.5	1.7	0.9
n-butyl acetate	0.06	-0.03	0.6	0.6	51.7	25.9
Cellosolve acetate	0.03	0	0.3	0.1	9.6	5.2
Acetone	0.04	0.04	0.2	0.1	134.4	85.8
Cyclohexanone	0.02	-0.03	0.3	0.2	D**	D
Strong Hydrogen Bonding						
Isopropyl alcohol	0	-0.04	0.02	0	0	0

Table 2 Continued. Swell Index of Various Plastics Before and After Argon Gas Plasma Treatment*

Solvent	Polyester		Polysulfide		PC Board	
	Before	After	Before	After	Before	After
Weak Hydrogen Bonding						
Heptane	0	0.02	0	-0.5	0.03	0.02
2-ethylhexylchloride	0.01	0.04	0	0.7	0.06	0
Trichlorotrifluoroethane	-0.03	0.03	0.13	-0.06	-0.02	0.02
Methylchloroform	0.01	0.06	47.1	53.1	0.02	0.02
Toluene	0.06	0.07	50.6	34.8	0.03	0
Trichloroethylene	0.34	0.42	248.3	148.9	0.10	0.15
Perchloroethylene	0.06	0.03	20.1	10.3	0.01	0
Methylene Chloride	2.84	1.75	298.8	275.6	0.4	0.18
Vinyltrichloride	0.65	0.65	406.2	390.8	0.10	0.1
Moderate Hydrogen Bonding						
2-ethylhexyl acetate	0.02	0.01	0	1.4	0.23	0.2
n-butyl acetate	0	0.04	15.1	15.69	0.01	0
Cellosolve acetate	0.02	0.04	38.5	41.2	0.10	0.04
Acetone	0.14	0.06	11.0	14.6	0.07	-0.04
Cyclohexanone	0.01	0.02	156.2	153.7	0.03	0
Strong Hydrogen Bonding						
Isopropyl Alcohol	0.02	0.02	0	0.05	0.01	0.02

Table 2 Continued. Swell Index of Various Plastics Before and After Argon Gas Plasma Treatment**

Solvent	Diallylphthalate		Phenolic		Urethane	
	Before	After	Before	After	Before	After
Weak Hydrogen Bonding						
Heptane	0	0.01	0	0.33	2.27	1.9
2-ethylhexylchloride	0	0.02	0	0.31	7.65	7.5
Trichlorotrifluoroethane	0.09	0.02	0.4	0.38	6.59	6.5
Methylchloroform	0	0.04	0	0.33	37.85	54.4
Toluene	0	0.03	0	0.32	41.82	35.3
Trichloroethylene	0	0.2	0	0.36	101.69	102.6
Perchloroethylene	0.07	0.03	0.4	0.32	39.65	37.2
Methylene Chloride	0.29	3.30	0.3	0.44	145.7	151.8
Vinyltrichloride	0.01	0.30	0	0.34	128.32	143.2
Moderate Hydrogen Bonding						
2-ethylhexyl acetate	0	0.04	0	0.29	11.09	7.75
n-butyl acetate	0	0.02	0	0.23	22.82	23.72
Cellosolve acetate	0	0.04	0	0.24	17.61	19.9
Acetone	0	0.13	0	0.36	24.63	23.1
Cyclohexanone	0	0.02	0	0.19	47.67	52.4
Strong Hydrogen Bonding						
Isopropyl alcohol	0	0.01	0	0.22	0.39	5.9

Table 2 Continued. Swell Index of Various Plastics Before and After Argon Gas Plasma Treatment*

Solvent	Nylon		Mylar		Polycarbonate	
	Before	After	Before	After	Before	After
Weak Hydrogen Bonding						
Heptane	0.15	-0.01	0.4	0.11	0.04	0.03
2-ethylhexylchloride	0.16	-0.02	0.6	0.12	0.01	0.06
Trichlorotrifluoroethane	-0.11	-0.02	1.3	-0.11	0.07	0.03
Methylchloroform	0.11	0	0.4	0	33.3	29.06
Toluene	0.17	-0.02	0	-0.25	26.1	20.22
Trichloroethylene	0.15	0.25	2.3	1.67	D**	D
Perchloroethylene	-0.08	0	0.13	0	3.21	2.26
Methylene Chloride	2.8	1.56	7.3	3.39	D**	D
Vinyltrichloride	0.10	0.15	6.5	5.63	D**	D
Moderate Hydrogen Bonding						
2-ethylhexyl acetate	0.10	0.10	0.98	0.12	0.3	0.41
n-butyl acetate	0	0.12	0.5	0	10.3	9.86
Cellösolve acetate	0	0.12	0.6	0	15.9	17.95
Acetone	0.05	0.09	1.5	0.47	17.5	16.61
Cyclohexanone	0	0.10	0.6	0	D**	D
Strong Hydrogen Bonding						
Isopropyl alcohol	0.26	0.06	0.5	0.27	0.01	0

*Test conditions: 30 minutes, 25 W, 500 cm³/minute gas flow.

**D = dissolved.

Table 3. Changes in Plastic Swell Index After Argon Gas Plasma Treatment

No Change	Reduced Solvency		Increased Solvency
	Minor	Moderate	Minor
Phenolic	Nylon	Polyvinylchloride	Teflon
	Polyethylene	Polysulfide	Diallylphthalate
	Polycarbonate		Urethane
	Polyester		
	Printed Circuit Board Laminate		
	Mylar		

energies are dissipated by physical effects such as ablation and electrostatic charging, while optical radiation can provide polymer-free radicals.⁹ If ablation had occurred to expose sub-surface layers of the printed circuit board laminate, compositional changes of the surface would have been shown by all three radio-active surface energy probes. Similarly, the probes would have responded to decomposition of the surfaces by the optical radiation. However, changes to the plastic laminate and to the metal were recorded by Meseran analysis using the moderately polar diethyl succinate, while little or no change occurred with the nonpolar tridecane and the weakly polar tetrabromoethane. This effect was seen with argon, regardless of gas flow (Figures 9 and 10). It also was observed with oxygen at lower gas flow and wattage levels (Figures 11 and 12).

The data suggest, in the case of printed circuit board materials and under the conditions of this evaluation, that plasma causes surface changes which include modification of the electronic state of the surface. The surface energy of plastics is a result of the van der Waal's attraction forces that occur between molecules, while metals involve ionic forces. Thus, plasma excitation of plastic surfaces may be due to induced dipole activity to show increased polarity, while electron buildup or alignment occurs with metals. Dipole moments are a measure of the electrostatic imbalance of a molecule. Dipole-dipole, dispersion, and induction

KAPTON

POLYETHYLENE

MYLAR

POLYESTER (FIBERGLASS FILLED)

Figure 8. Contact Angle Indications of Surface Activity Life After Argon Plasma Treatment of Plastics

POLYVINYL CHLORIDE

DIALLYLPHTHALATE

EPOXY (FIBERGLASS FILLED)

CELLULOSE ACETATE

Figure 8 Continued. Contact Angle Indications of Surface Activity Life After Argon Plasma Treatment of Plastics

Figure 9. Effect of Argon Plasma on Surface Activity of Printed Circuit Board Laminate

interaction energies all decay with the increasing sixth power of the distance of separation.¹⁰ Plasma may have increased the activity distance.

If the change in the plastic or metal surface were permanent, the Meseran level would not change. However, the Meseran level does return to its original value, which suggests that the activity of the plasma treated surface is temporary (Figure 13) and is supported by contact angle data (Table 4). Conditions of ablation, decomposition, scissioning, or cross-linking would cause permanent Meseran changes. An excited dipole or electronic state, however, could very easily be dissipated or stabilized in time without disturbing the chemical nature of the surface.

Figure 10. Effect of Argon Plasma on Surface Activity of Printed Circuit Board Tinned Copper

Ion Current Density

For a particular size and geometry of gas plasma chamber, process conditions must be determined to obtain optimum plasma effects on surfaces. Gas flow can control the dilution or concentration of the ion current density of the plasma at the surface of the solid it contacts. This work involves RF plasma with the solid considered as floating (no direct ground). Meseran data can be used to measure the process conditions which yield the greatest surface activity, presumed to be caused by the greatest ion current density, reflected by Meseran measurements (Figure 5).

ACCOMPLISHMENTS

The fact was determined that printed circuit board laminates are not adversely affected by argon gas plasma over a wide range of process variables of time and gas flow. Oxygen plasma, on the other hand, causes erosion, crevices, and resin removal to occur, depending upon the degree of the surface treatment.

Figure 11. Effect of Oxygen Plasma on Surface Activity of Printed Circuit Board Laminate

Meseran analysis has shown that argon-plasma-treated printed circuit board laminates retain their surface activity more than twice as long as oxygen treated surfaces. Argon treated laminates are still fairly active after 14 days, while oxygen treated laminates become inactive in less than 5 days.

Figure 12. Effect of Oxygen Plasma on Surface Activity of Printed Circuit Board Tinned Copper

Process parameters for providing optimum surface activity for optimum adhesion potential of printed circuit boards without laminate damage are tentatively established as argon plasma treatment of 30 watts, 100 to 200 cm³/minute gas flow, and 10 to 20 minutes for metals and plastics; and 50 to 200 watts, 100 to 200 cm³/minute gas flow, and 10 to 30 minutes for metals only. Optimum surface activity should relate to adhesion potential. Establishing process time with optimum process conditions will yield efficient removal of organic contamination.

The effectiveness of plasma in removing contaminants is controlled by the concentration and physical nature of the contaminant (cured, semisolid, liquid), based on another study.⁸ Process parameters to remove unknown contaminants require a more extensive evaluation.

Figure 13. Surface Activity of Printed Circuit Board Laminate After Plasma Treatment

FUTURE WORK

The following items are recommended for consideration for further studies concerning both the use of plasma for contaminant removal, and its effect on surfaces.

Establish an argon or oxygen plasma process which will effectively remove typical organic contaminants associated with manufacturing processes.

Define organic contaminant removal according to concentration, physical type of contaminant (solid, semisolid, liquid), plasma process conditions, and process time.

Evaluate surface leakage and voltage breakdown (arc-over) after plasma treatment of printed circuit boards.

Table 4. Life of Plasma Treated Printed
Circuit Board Laminate

Condition of Laminate	Contact Angle for Indicated Surface	
	Argon-Treated (Degrees)	Oxygen-Treated (Degrees)
As Received	110	110
After Plasma Treatment	10	10
After Aging		
5 Days	10	70
12 Days	50	105
19 Days	90	110
26 Days	105	110

Characterize surface changes of a variety of plastics and
surface activity life after plasma treatment.

Evaluate ion current density conditions for any new plasma
equipment used. Faraday cups are recommended.

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