proceedings

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This publication is a compilation of the papers presented at the 30th Annual National Relay Conference held at Oklahoma State University April 27 and 28, 1982. This conference is co-sponsored by the National Association of Relay Manufacturers and the Oklahoma State University School of Electrical Engineering.

This conference endeavors to provide a forum for the open exchange of information between relay manufacturers and users and the frank discussion of their mutual problems with the objective of improving the manufacturer's ability to supply reliable relays to meet the user's requirements and to help the user properly apply relays.

Papers presented at the conference are screened by a Paper Selection Committee composed of members from relay users, manufacturers, and educators. An expanded abstract of each paper is evaluated by the committee, and those meeting certain standards of quality and technical excellence and possessing the most potential benefit to the relay industry are selected for the program. The author and his affiliation remain anonymous in the selection of the papers.

Special recognition is hereby made to the authors, for without their effort in preparing and presenting their papers, this publication would not be possible. Our appreciation is also expressed to the staff of the Office of Engineering Extension for their work in arranging for the facilities and for supervising the development and sending of the conference publicity. We also express our appreciation to Professor Dan Lingelbach and the School of Electrical Engineering who have continually devoted untiring efforts toward conducting increasingly beneficial conferences each year.

The 31st Annual National Relay Conference is scheduled for April 25, 26 and 27, 1983, at Oklahoma State University.

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1981 AWARDS

The National Association of Relay Manufacturers, in recognition of the outstanding work of the following authors in preparing and presenting their papers, bestowed the honorary award, "Fellow in the College of Relay Engineers", to them at the 1981 Conference.

Alan W. Wisniewski*
John A. Buono
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"USE OF SURFACE ANALYSIS IN DIAGNOSING RELAY PROBLEMS"

Steen Bentzen General Radio, Inc. West Concord, Massachusetts

Edward F. Sutherland Relay Testing Services, Inc. Wolfeboro, New Hampshire

"ENHANCING RELIABILITY
OF DRY REED RELAYS
USED IN AUTOMATIC TEST EQUIPMENT"

Takeshi Sasamoto
Haruzo Semda
Tomomi Umemoto
Tetsuo Omamiuda
Nippon Electric Company, Ltd.
Tokyo, Japan

"REED CONTACT FOR LARGE SURGE CURRENT LOAD"

B. M. Tieman Philips Gloeilampenfabrieken N.V. Heerlen, The Netherlands

"THE CHARACTERISTIC LIFE
OF A DRY REED CONTACT-THE INFLUENCE OF SWITCHING PHENOMENA"

M. J. Pike-Biegunski Englehard Industries Division Englehard Minerals & Chemicals Corp. Menlo Park, Edison, New Jersey

"EVALUATION OF THE ELECTRICAL RESISTANCE OF LIGHT DUTY CONTACTS USING STATISTICAL ANALYSIS"

^{*}The NARM Charles Schneider Best Paper Award of \$500 was awarded to Alan W. Wisniewski, John A. Buono, and W. Scott Andrus

Session Chairmen





Smith

Scandora

Tony Scandora began his career in the relay industry in 1946 as Sales Manager in the relay division of Wells Sales, Inc. In 1951, he became Vice President and General Manager of Relay Sales, Inc., the first major distributor of relays.

After a year at C. P. Clare in 1961, he joined with a group that started Mossman-Elliott Corp. and served as Sales Manager and Chief Engineer. In 1965, he started United Controls Corp. and specialized in the manufacture of telephone type relays.

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He is currently serving as a Director of NARM, and is a member of IEEE.

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Mr. Smith attended Rutgers University, New Brunswick, N. J. and completed his E. E. studies at Newark College of Engineering in Neward, N. J. The author of numerous articles on solid state switching, an author at the 28th. and 29th. NARM conferences and a contributing author to a number of books on solid state devices. He also lectured extensively in the Middle East, Europe, U. K., Canada and the United States.



Harkness



Lorenz

STRESS RELAXATION OF BERYLLIUM COPPER STRIP IN BENDING

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Mr. Lorenz is a graduate of Tri State College with a degree in Mechanical Engineering.

SOFT FERROMAGNETIC MATERIALS AND HEAT TREATMENT

By John Schmidt, Jr., Chief Relay Engineer, Guardian Electric Manufacturing Company, Chicago, Illinois 60607; and Jerome V. Bell, Metals Technology Corp., Addison, Illinois.

John received a BS degree in Electrical Engineering from Northwestern University in 1942. Upon graduating, he joined Guardian Electric Manufacturing Company, in Chicago, Illinois, becoming Chief Engineer in 1957. From 1968 to 1976 he was Director of Engineering for Littel-Fuse, Inc., in Des Plaines, Illinois. From 1976 to 1979 he was Product Development Supervisor for the Eaton Corporation in Carol Stream, Illinois. John rejoined Guardian in 1979 as Chief Relay Engineer. He is a member of IEEE and also an active participant in the affairs of SAE; A2R Relay Sub-Committee.

Jerome V. Bell, Sr. received his B.S. degree in chemistry from the Ohio State University in 1949. He published two papers on infra red spectroscopy, and was co-inventor of six patented chromizing processes.

In 1963 he founded a specialty heat treating company known today as the Metals Technology Corporation, Addison, Illinois.







Bell

PROPERTIES OF BERYLLIUM COPPER C17510 FOR HIGH CONDUCTIVITY APPLICATIONS

By Amitava Guha, Senior Research Metallurgist, Alloy R & D, Brush Wellman, Incorporated, 17876 St. Clair Avenue, Cleveland, Ohio 44110.

Dr. Amitava Guha is Senior Research Metallurgist in the Alloy Research and Development Department, Brush Wellman, Incorporated, where he is engaged in materials development and the physical metallurgy of copper-base alloys. His MS and PhD degrees, both in Metallurgy, are from Carnegie-Mellon University and the University of Pittsburgh, respectively. Dr. Guha is a member of the ASTM Committee E28.10 on Standard Methods of Bend Testing for Spring Applications.

THE DESIGN AND DEVELOPMENT OF A MINIATURE MERCURY WETTED TRANSFER CONTACT RELAY

By Robert N. Rath, Associate Member of Technical Staff, Bell Telephone Laboratories, Inc., Columbus, Ohio 43213.

Mr. Rath is an Associate Member of the Technical Staff in the Specialized Components Development Group at Bell Telephone Laboratories in Columbus, Ohio. After graduating from Penn. Technical Institute, Pittsbugh, Pa. in 1966, he joined Bell Labs where he currently has engineering responsibility for mercury wetted sealed switches. Previous responsibilities include life and environmental testing of electro-mechanical apparatus and separable connectors.

A PLASTIC-ENCAPSULATED, ELECTROMECHANICAL RELAY FOR APPLICATIONS IN TELEPHONY

By Jan Kafka, Chief Engineer of the Electrophysical Laboratory, Telephone Switching Product / ITT - Standard Telephone & Radio, Zurich, Switzerland, 8055.

Jan Kafka completed an Advanced Technical Apprenticeship in communications engineering in Prague and also engaged in special studies of environmental influences on electronics products. 1951 thru 1962 he was employed as a designer of components used in telephone exchange technilogy, and then as the head of the laboratory dealing with the environmental resistance of components and equipments with the TESLA company in Prague. Since 1969 he has been Chief Engineer in the Electrophysical Laboratory of the Telephone Switching Product Line of ITT-STR, Zurich.

He is a member of the Swiss Electrotechnical Association and of the Swiss national committee on IEC TC 41, Relays.

Guha



Rath



Kafka

RELIABILITY OF THE PLASTIC-SEALED RELAY

By Kazuhisa Yoshida and Shigeru Tajima, Matsushita Electric Works, Ltd., 1048 Kadoma, Kadoma-shi, Osaka, 571 Japan.

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He is a member of the Institute of Electronics and Communication Engineers of Japan.

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He is now Engineering Manager of Relay Development Department, Precision Electric Controls Division.

CONTACT ASSESSMENT OF PLASTIC SEALED RELAYS IN LOW ENERGY CIRCUIT APPLICATIONS.

By Herman J. Desmet, Interconnection Technology, Northern Telecom Ltd., P.O. Box 3511, Station C, Ottawa Ontario, Canada K1Y3HC.

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He has worked in the comm. field in Northern Elec. Co., BNR and Northern Telecom since 1960.

From 1964 - 1970 he was in charge of the design of a min. crossbar switch MINIBAR switch.

Since 1970 he has been responsible for several programs on relay contact, connector and interconnection programs.

More recently he has been in charge of the engr. to apply plastic sealed relays in DMS type comm. systems.

He is a professional engineer in the province of Que. and a member of the ASTM Committee B4.



Yoshida



Tajima



Desmet

RELIABILITY TESTING OF OPEN CONTACT RELAYS

By Tommie J. Wallace, Senior Development Engineer, Western Electric Company, Columbus, Ohio 43213.

Tommie J. Wallace (Tom) is a Senior Development Engineer, employed at the Western Electric Company since Septemer 1959. He has held significant development assignments associated with Electro Mechanical Switches and Relays. These assignments included contributions in development of new products as well as the implementation of Cost Reduction, improvements to manufacturing processes and the maintenance of manufacturing processes and the maintenance of manufacturing specifications and layouts. From March, 1977 to May 1978 he worked with Bell Telephone Laboratories on the design and development of a new relay to meet a Bell System need for a new product line. His current assignment is the coordination of the production of this new relay and to maintain the manufacturing specifications. He is also presently responsible for forecasting demands and the reliability testing for all relays manufactured at the Columbus Works.

COMPUTER UTILIZATION FOR RELIABILITY TEST METHODS OF ELECTROMAGNETIC RELAYS

By Kunio Mano, Professor and Doctor, Graduate School of Engineering, Meijyo University, Nagoya, 468 Japan; Taiji Hosaka, Student, Yoshihiro Inoguchi, Student, and Toshiaki Eguchi, Student, Graduate School of Engineering, Meijyo University.

Professor Kunio Mano was born in Aichi Prefecture, Japan on September 29th, 1910. He received the B.S. and Ph.D. degrees in Electrical Engineering from Tohoku University, Sendai, Japan, in 1937 and 1960 respectively.

In 1948, he became an Assistant Professor, and in 1954 he became a professor in the Department of Electrical Communication Engineering, Tohoku University. In 1974, he was made a Professor Emeritus of Tohoku University. In 1974, he was made a Professor in the Department of Electrical Engineering and the Graduate School of Engineering of Meiiyo University.

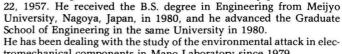
Dr. Mano is a senior member of IEEE, the Institute of Electronics and Communication Engineers of Japan, the Society of Instrument and Control Engineers, and so on.

Dr. Mano has been active academically in the Electronics and Electrical Engineering field. He was awarded a Violet Ribbon Medal from his Majesty the Emperor for his work and also received the Ragner Holm Scientific Achievement Award.

Taiji Hosaka was born in Aichi Prefecture, Japan on October 9th, 1957. He received the B.S. degree in Engineering in 1980, and he advanced the Graduate School of Engineering in Meijyo University in 1980.

He is studying the reliability of electromechanical components in Mano Laboratory.

Mr. Hosaka is a student member of IEEE, and an associate member of the Institute of Electronics and Communication Engineers of Japan.



Yoshihiro Inoguchi was born in Shizuoka Prefecture, Japan on October

tromechanical components in Mano Laboratory since 1979.

Mr. Inoguchi is a student member of IEEE, and an associate member of the Institute of Electronics and Communication Engineers of Japan, he is also an associate member of the Institute of Electrical Engineers of

Toshiaki Eguchi was born in Aichi Prefecture, Japan on November 2, 1957. He received the B.S. degree in Engineering from Meijyo University, Nagoya, Japan, in 1981, and he advanced the Graduate School of Engineering in Meijyo University in 1981.

He is studying the bounce effect of contact and the life reliability of opening and closing contact, and other contact phenomena in Mano Laboratory.

Mr. Eguchi is an associate member of the Institute of Electronics and Communication Engineers of Japan, and a student member of the Institute of television engineers of Japan.

HIGH STABILITY CONTACT RESISTANCE MONITORING CIR-CUITS

By James R. Morton, Manager of the Test Engineering Department, Elec-Trol, Incorporated, Saugus, California 91350.

Jim Morton received his B.S.E.E. with honors from New Mexico State University in 1975. Subsequently, he was employed by Rockwell International B-1 Bomber Division for one year, then moved to Bendix Electrodynamics Division. At Bendix, Jim performed analog and digital circuit design on sonar weapons systems for three years.

After Bendix, Jim was employed as a project engineer by FMC Agro-Electronics to complete development of a microprocessor-based tomato sorter. He is presently employed by Elec-Trol, Incorporated as Manager of the Test Engineering Department.

Jim enjoys family activities with his wife and two sons. His remaining time is taken up by flying, photography, and target shooting.

A RELAY TREE APPLICATION AND ITS DESIGN

By Vicki L. Mitchell, Product Manager - Components; and L. J. Seiden, Vice President, Research and Engineering, T-Bar, Incorporated, Wilton, Connecticut 06897.

Vicki Mitchell was born in Sturgis, South Dakota in 1954. She received her Bachelor of Business Administration Degree from Western Connecticut State College.

She is presently Components Product Manager at T-Bar, Incorporated. Mrs. Mitchell resides with her husband and son in Norwalk, Connec-



Wallace



Mano



Hosaka



Inoguchi



Eguchi



Morton

Born in New York City, New York, in 1929, Mr. Seiden received his B.E.E. from CCNY, and his M.E.E. from CUNY. He is currently Vice President of Research and Engineering at T-Bar, Incorporated, Wilton, Connecticut.

Mr. Seiden holds eight (8) United States and sixteen (16) foreign patents for switching devices and products from the component to the system level.

Before joining T-Bar, Inc., he held management and engineering positions in controls with AMF in Stamford, Connecticut, and with Grumman in Bethpage, New York.

THE PROGRAMMABLE CALCULATOR AS A POWERFUL RELAY DESIGN AND APPLICATION TOOL

By Robert Filchak, Project Engineer, Potter & Brumfield Div., AMF Incorporated, Princeton, Indiana 47671.

Mr. Filchak received a B.S.E.E. from Purdue University. He worked for a number of years for P.R. Mallory in the testing and application of electrical contacts, for RBM Division of Essex International on blanket thermostats and controls, and for Mechanical Products on motor protectors, commercial circuit protectors, and aircraft circuit breakers. He was the project engineer for all circuit breakers on the Apollo and LEM spacecraft. He has been with Potter & Brumfield for the last nine years, working on thermal and magnetic circuit breakers.

PREVENTION OF ELECTROSTATIC DAMAGE DURING THE MANUFACTURE OF TIME DELAY RELAYS

By Ed Rauch, Magnecraft Electric Co., Chicago, Illinois.

Ed Rauch is a Product Manager at Magnecraft Electric Company. He graduated from the Illinois Institute of Technology in 1968, with a Bachelor of Science degree in Electrical Engineering, and in 1973 received his Masters Degree in Business Administration from the University of Illinois. He has spent the last 10 years in electronic design and application with Westinghouse, Motorola, and BRK Electronics. He is presently responsible for the engineering and production of time delay and solid state relays at Magnecraft Electric Company, 5575 North Lynch Avenue, Chicago, I. 60630.

THE STATISTICAL APPROACH TO QUALITY WHAT? WHY? AND SHOULD WE?

By Carl B. Knox Jr., Plant Manager, Potter & Brumfield Division AMF Incorporated, San Juan Capistrano, California 92675; and Harry D. Sauter, Director, Quality Assurance, Potter & Brumfield Division, AMF Incorporated, Princeton, Indiana 47670.



Mitchell



Mr. Knox is currently Plant Manager for the San Juan Capistrano Plant of Potter & Brumfield Division of AMF Inc. In this capacity he is responsible for the operation of the California Plant. Currently he is Vice-President of Technical Activities for NARM. Mr. Knox authored six technical papers for the Annual Relay Conference. Three times elected "Fellow in the College of Relay Engineering", and won the "Charles Schneider Best Paper Award". He has authored various technical magazine articles. Mr. Knox has served as Session Chairman, on the Paper Selection Committee and as an Awards Judge for the Annual Relay Conference. He has contributed to the preparation of the NARM Engineers Relay Handbook. He was presented the "Key Man Award" at Babcock Electronics Corp. Mr. Knox was a guest lecturer at an Electronic Seminar held at Purdue University, Hammond, Indiana.

Harry D. Sauter is Director, Quality Assurance, for Potter & Brumfield Division, AMF Incorporated. Prior to joining P&B in 1959 he spent eight years with American Kitchens Division of AVCO where he was manager of engineering services for ordance research and development projects.

Mr. Sauter graduated from Purdue University in 1950 with a BSEE in electrical power. He is an ASQC Certified Engineer and Director-at-Large for the American Society of Quality Control. He has presented papers and spoken at many Quality Control conferences and seminars.

"PRODUCTIVITY ACTION TEAMS: AN AMERICAN INVOLVE-MENT STRATEGY"

By **D. Scott Sink**, Assistant Professor, Industrial Engineering and Management, O.S.U., Stillwater, Oklahoma 74078.

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Filchak



Rauch

THE TRAN-TROL TM DEVICE: COMBINING ELECTROMECHANICAL SWITCHING AND POWER TRANSFORMATION IN THE SAME COMPONENT

By John J. O'Farrell, President, The TRAN-TROL $^{\rm TM}$ Company. Tucson, Arizona 85712.

Mr. O'Farrell is a graduate of the New York Technical Institute of New Jersey. He joined IBM as a draftsman in their Product Development Laboratory in 1941 at the age of 17.

During a 30-year tenure at IBM, with a leave of absence for military service in the U. S. Army Signal Corps during World War II, he worked on projects in development and production engineering and manufacturing, engineering management, corporate staff, and marketing systems engineering. He took early retirement from IBM in December 1971.

In January 1973, Mr. O'Farrell joined Computer Services. The City of Tucson, Arizona. As Systems Analyst, he was responsible for design and implementation of computer systems in areas of government finance, geographic and census data, public library, and public housing. He left The City in August 1979 to start his own consulting service in computer applications and systems design and to continue the developmental work on the TRAN-TROLTM device.

Mr. O'Farrell authored a number of papers during his tenure with IBM and holds a U. S. Patent on his transformer/switch device.

CORROSION OF ELECTRICAL CONTACT MATERIAL

By **Satya P. Sharma**, Supervisor, Bell Telephone Labs, Columbus, Ohio 43213.

Satya Sharma is supervisor of the Connector Technology Group at Bell Laboratories. He holds a Ph.D. from the University of Pennsylvania and joined Bell Labs in 1970. He is a sponsible for basic studies of the mechanisms which affect contact behavior and reliability, for the development of accelerated corrosion tests and for the evaluation of new connector technologies. He has published more than 50 research papers in areas of contact physics, material science and applied mechanics.



Knox,



Sauter



Sink,



O'Farrell



Sharma

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CORROSION OF ELECTRICAL CONTACT MATERIALS

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Abstract

Most electrical contacts employ a precious metal layer over a base metal as the contact material. Exposure of the base metal due to wear or diffusion through the precious metal layer and its subsequent reaction with the environment may result in the formation of a tarnish film in the contact area; this film may cause high Contact Resistance (CR). In indoor low Relative Humidity (RH) ambients, the films are primarily oxides of base metals with small amounts of chlorides and sulfides; no pore or creep corrosion is observed in low RH ambients. The absence of pore and creep corrosion is due to the passivity of the oxide film.

Precious metals like Pd and Ag and their alloys may form tarnish films in high RH ambients. These films are chlorides of Pd on Pd and PdAg alloys and may result in high CR. Relative humidity plays a significant role in the tarnishing behavior of Pd and its alloys.

Adsorption isotherms as a function of RH on various materials show that less than a monolayer of water is adsorbed at RH < 20 percent but more than a few monolayers of water are adsorbed at RH > 60 percent. Pollutants present in the atmosphere react rapidly with the materials in the presence of few monolayers of water.

Introduction

Various electrical contacts used in the electronics industry (e.g., in separable connectors), employ a precious metal layer over a base metal substrate as the contact material. The purpose of the precious metal is to eliminate or reduce the tarnishing of the contact surface. Traditionally, gold plating has been used as the contact material. Exposure of the base metal due to wear processes or diffusion through the gold layer and its subsequent reaction with the environment may result in forming a tarnish film in the contact area; this film may

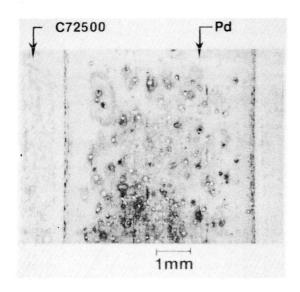
cause high contact resistance. This situation is different compared to various other industries where thick adherent films which protect the metal may be beneficial and only very thick corrosion films which cause the loss of material, are considered detrimental. In the electrical contact industry, films of the order of few hundred A thick can cause high Contact Resistance (CR). Consequently, the study of corrosion or tarnishing of electrical contacts requires the fundamental understanding of the material and environmental interactions in the beginning stages. The purpose of this report is to describe the present understanding of the environmental interactions with materials employed in the contact industry.

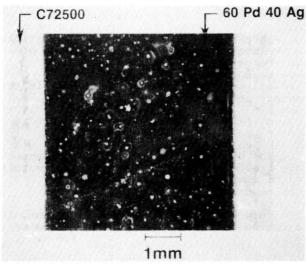
Corrosion Mechanisms

The corrosion mechanisms operative in thin precious metal platings on base metals can be classified into several subcategories.

- a. Pore corrosion In pore corrosion, the corrosion of base metals at the bottom of a pore in the plating takes place. 2,3,4,5 This mechanism may be important in thin porous platings in severe ambients. The corrosion products mushroom out of the pores and spread on to the plated surfaces causing high CR. An example of pore corrosion is shown in Figure 1, where two precious metals, Pd and 60Pd40Ag over Ni over a Cu alloy (CDA 725), were exposed to high concentration of Cl₂ at high Relative Humidity (RH). Severe pore corrosion is seen on these samples.
- b. <u>Creep Corrosion</u> If a base metal is in lateral contact with a precious metal layer, the corrosion of the exposed base metal takes place and some of the corrosion products migrate over the precious metal surface and may cause high CR in the contact region. This migration of corrosion products is called creep corrosion. ^{6,7}

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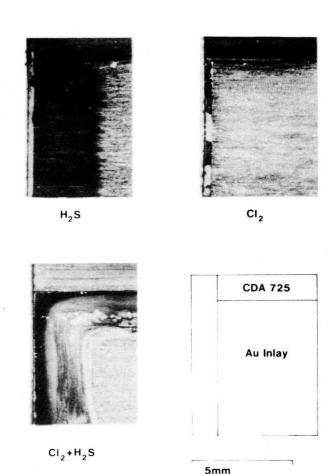




Pd and 60 Pd 40 Ag 50μ in Inlay Exposed 14 Days to Wet Chlorine at 2 to 10 ppm Level Figure 1

Figure 2 hows this type of corrosion on a gold inlay in lateral contact with CDA 725 in three ambients containing high concentrations of $\rm H_2S$, $\rm Cl_2$, and $\rm Cl_2+H_2S$ in high relative humidities.

- c. Corrosion of Impurities There may be certain impurities incorporated in the precious metal layer, such as Co and K, etc., coming from the plating bath. 8,9,10 Oxidation of these impurities may cause a surface film and cause high CR.
- d. Substrate Corrosion Diffusion of substrate material through the precious metal layer may take place (for example, Cu through Au) if the operating temperatures



Effect of Three Ambients on 50μ Inch Gold Inlay (80 RH) Figure 2

are high enough. 11,12,13 The subsequent oxidation of the substrate material may cause a resistive surface film.

e. Corrosion of Wear Induced Exposed Base Metals - If the contact surfaces are mated and unmated several times or a switch is operated several times, wear through of the plating may take place and the base metal may be exposed to the atmosphere and tarnish. This may also cause high CR.

In all of these mechanisms, the atmospheric corrosion of the base metal is responsible for the degradation of the contact performance.

f. Corrosion of Contact Material - In certain cases, materials other than gold are employed as the contact finish in electrical contacts; for example, silver and Pd and their alloys. Silver may tarnish and may form silver sulfide and chloride films. 14,15,16 Pd and its alloys may also form PdCl 2 film in certain high RH environments. 17,18

In a field studies program conducted at Bell Telephone Labs, it has been determined that the films which form on base metals in indoor sites are primarily oxides together with small amounts of chlorides and sulfides. ¹⁰ In most indoor sites, pore and creep corrosion are not observed. ^{19,20} The reason for the absence of pore and creep corrosion is that most of the indoor sites have low relative humidities (less than 55 percent) and at these low relative humidities the films which form

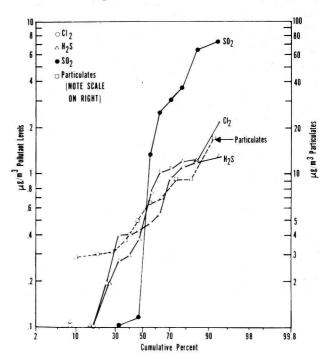
(predominantly oxides) do not creep. 6,7 The sulfides and chlorides are the migrating films. Oxides act as passive films against sulfidation and chlorination of the base metal surfaces. 7,21,22 However, if the RH is high, the oxides no longer act as passive films and pore and creep corrosion may take place. 21,22 This may be especially true in nonair-conditioned sites or outdoor sites.

The major constituents of the atmosphere are oxygen, nitrogen, and water vapor. There are small amounts of oxides of nitrogen, sulfur dioxide, H₂S, elemental sulfur, Cl₂, chlorine containing compounds and particulates. Hydrogen sulfide, sulfur dioxide and chlorine (including chlorides) in the presence of high RH are the most corrosive reactants of the atmosphere. The concentration of these gases in telephone central offices is in the few ppb range ²³ as shown in Figure 3; however, these small concentrations can cause significant corrosion problems in the presence of high RH.

Experimental Techniques

In understanding the tarnishing of electrical contacts, the measurement of contact resistance by the four wire probe has been used extensively by various investigators. 24 This technique is a sensitive measure of the presence of films on the contact surface and is a quantity of real interest in electrical contacts. However, this technique sheds no light on the thickness, chemical and elemental identification, and the film morphology. Auger electron spectroscopy (AES) and ESCA are utilized for chemical and elemental identification; SEM is used for the film morphology, and AES with sputter back profiling and cathodic reduction are used for film thickness measurements. The quartz crystal microbalance coupled with a permeation tube apparatus is used to measure the kinetics of film growth. 18,22 The materials of interest are vacuum deposited on an AT cut quartz crystal. If the material corrodes, the crystal gains weight and its frequency decreases. By measuring the change in frequency, the extent of the corrosion can be determined. For one Hertz

change in frequency, the crystal gains 1.77×10^{-8} gms of weight. The details of the quartz crystal microbalance in corrosion research are given elsewhere. 22



Pollution and Particulate Levels (Central Offices)
Figure 3

Passivity of Oxide Films on Base Metals

As mentioned earlier, in field studies conducted at Bell Labs, no creep or pore corrosion has been observed on connector products and base metal coupons plated with gold and exposed in indoor ambients. 19,20 While the relative humidity in indoor sites generally remains low (<55 percent), 23 there are instances when the RH could be higher. The absence of pore or creep corrosion was attributed to the passivity of oxide films²² which grow on base metals, i.e., Cu,O and NiO. An oxide film grows on the exposed base metals and this naturally grown oxide inhibits the growth of sulfide films on the base metals. In addition, it is seen that the major constituent of the film on base metals in most indoor sites is the oxide with only small amounts of chlorides and sulfides. 14 The passivity of oxide may also explain this observation. Experiments have been conducted in the lab to prove this hypothesis.

Samples of electron beam evaporated copper on AT-cut quartz crystals were prepared. Some of these samples were preheated in air to produce ~225A of oxide

and others were heated in pure oxygen ambient to produce ~300-400A of oxide. These samples were exposed to varying relative humidities and known concentrations of pollutant gases in an apparatus shown schematically in Figure 4. A measured amount of dry air flows over a permeation tube containing the pollutant and kept at constant temperature. The pollutant diffuses out from the tube at a constant rate. Part of the air flows through a bubbler and is mixed with dry air to produce high or low RH air. By mixing appropriately, we can have air with different levels of pollutants and different RH. The samples are suspended in a reaction chamber and the growth rate of the film is monitored by recording the frequency change as a function of time with the help of a computer through a suitable interface.

Figure 5 shows the growth rate of the film as a function of time when the preoxidized Cu samples ²² and bare Cu samples are exposed to high concentrations (~5 ppm) of H₂S. It is seen that on preoxidized Cu samples, very little sulfide film forms at low RH as seen in curve A; on bare Cu, the

growth rate is linear with time at 0 percent RH (curve B). Thus an oxide film prevents the sulfidation of Cu at low RH. Curve D represents the growth of Cu₂S on bare Cu at 80 percent RH. The initial growth rate is ~4 times the growth rate at 0 percent RH on bare Cu. At the same RH of 80 percent, the oxidized Cu shows the growth rate of film to be slightly lower than on bare Cu. Thus, at high RH, Cu₂O does not completely protect Cu from sulfidation. The adsorption of water plays a dominant role in destroying the passivity of Cu₂O at high RH. This experiment demonstrates that if there are oxides on the surface, further sulfidation is reduced and consequently pore and creep corrosion are not as significant, especially at low RH.

Corrosion of Pd Based Materials

Due to the high price of gold, alternate materials to replace gold in contact applications have attracted attention by several investigators. Palladium and Pd-Ag alloys have been mentioned in the literature to be quite

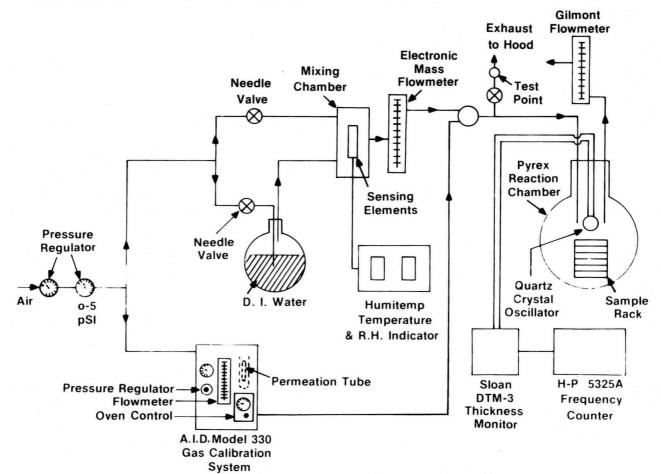


Figure 4

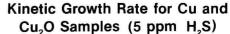
stable from an atmospheric corrosion point of view. In order to determine if these materials can be used in electrical contact applications, a field study program was initiated at Bell Labs to expose these

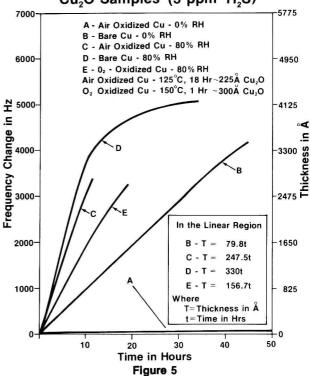
materials in different field sites. ²⁵ The samples investigated included Pd, 60Pd40Ag (R156) and 40Pd60Ag. These samples were brought back to the lab and were measured for CR increase, film thickness and film chemistry. The CR results have been

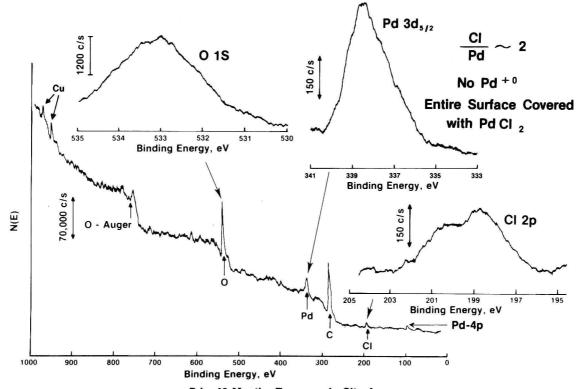
reported earlier by Antler. 25 It was found that Pd and R156 alloy have a reasonable CR behavior in air-conditioned (controlled) ambients. These materials develop high CR in uncontrolled (high RH) ambients coupled with chlorine containing species in the air. The chemistry of the film developed on these

samples was analyzed by ESCA. ¹⁷ Figure 6 shows ESCA spectra obtained from a Pd sample exposed in one of the uncontrolled indoor ambients. The Pd line occurs at 338.1 eV and the chlorine line at 198.4 eV. The shift of the Pd line by 3 eV from its elemental position of 335 eV suggests that Pd is chemically bonded to other elements, most probably to chlorine in PdCl₂ form.

The ratio of Cl to Pd, by taking into account the sensitivity factors, is found to be 2.0, further confirming this conclusion. We also find that the oxygen line in the spectra is associated with (OH). It seems that PdCl₂ is in the hydrated form (PdCl₂ '2H₂O).







Pd - 40 Months Exposure in Site A Figure 6

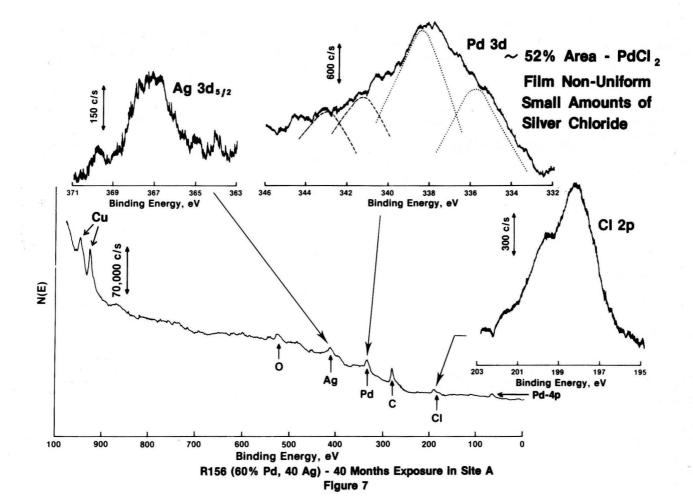


Figure 7 shows the results on 60Pd40Ag alloy exposed in the same ambient for the same amount of time. ¹⁷ In these spectra, the Pd peak can be deconvolved to yield two peaks, one at 338 eV and another at 335 eV. By quantitative calculation, it is determined that ~52 percent of the surface has PdCl₂ film. Comparing this sample with the Pd sample, it is seen that an alloy of 60 percent Pd 40 percent Ag is better than pure Pd from an atmospheric corrosion point of view.

In order to understand the formation of PdCl₂ on Pd, an experimental study was conducted where Pd coated quartz crystals were exposed to Cl₂ and HCl containing air at different RH. ¹⁸ The frequency change was converted to the weight gain due to tarnishing. Figure 8 shows the results of such an experiment. Some of the weight gain on the crystal is due to physical adsorption of H₂O and not due to the film formation. If this physically adsorbed water on the surface is excluded, the following picture emerges from this experiment. For HCl exposure even at high concentrations in the ppm range, no significant film forms on Pd

at high RH. At RH < 60 percent, ${\rm Cl}_2$ reaction with Pd proceeds slowly. At RH ~80 percent, the reaction with ${\rm Cl}_2$ proceeds at a high rate and almost linearly with time.

The effect of RH on the tarnishing of Pd by Cl₂ is very striking. If Pd is exposed to 1.8 ppm Cl₂ for 24 hours at various RH and the thickness of the film is plotted as a function of RH, it is seen that very little PdCl₂ film forms on the surface (Figure 9) for RH < 60 percent. ¹⁸ However, at RH > 60 percent, the film formation proceeds rapidly. These results have been confirmed by other techniques such as ESCA. RH of 60 percent can be termed as critical RH. The same kind of behavior is seen on other materials.

In other experiments, it has been shown that Pd does not react with salt in the presence of high RH. A model on the atmospheric corrosion of Pd and its alloys has been postulated to account for the field and the experimental results. It is felt that salts and other dust particles act as nucleation sites where water condensation

may take place at RH much less than 100 percent. The reaction of chlorine containing compounds takes place at these nucleation sites. $PdCl_2$ is hygroscopic and adsorbs two molecules of H_2O and further reaction takes place laterally until the entire surface is covered with $PdCl_2$ film. These films are thin but may be a cause of concern for use in the electrical contacts in uncontrolled indoor ambients.

Adsorption Isotherms - Corrosion Versus RH

In order to understand the basic corrosion mechanisms, one of the most important variables is RH. The corrosion depends upon the amount of water vapor adsorbed on a metal surface. The amount of adsorbed water increases with increasing RH. Utilizing the quartz crystal microbalance, the adsorption isotherms for various materials have been measured at different temperatures. Tyellow Figure 10 shows the weight gain (water adsorption) on a gold surface at different temperatures as a function of relative humidity (or relative vapor pressure). It is interesting to note that the amount of adsorbed water plotted as a function of RH does not change

significantly with temperature in the range of $15-60^{\circ}\mathrm{C}$.

Similar adsorption isotherms have been obtained for different materials by other investigators. 30 The amount of water in monolayers as a function of RH for a NiFe alloy, Fe, Ni, Au, stainless steel and Co has been measured by Phipps, et al. 30 No great differences in adsorption isotherms are seen from one metal to the other. It is seen that ~1 monolayer of water is adsorbed at ~25 percent RH. At RH > 60 percent more than 2 monolayers of water are adsorbed on all materials. These adsorption isotherms have been fitted to the BET isotherm model and the heats of water adsorption on various materials have been calculated by different investigators. 27,28,29,30 These heats of adsorption on Au, Cu, Cu,O, Fe, Co, Ni, NiO, Pt and Sn vary between 11.5 and ~13 Kcal/mole. The heat of vaporization of water is 10.5 Kcal/mole. The heats of adsorption on various materials, therefore, do not differ significantly from the heat of vaporization. These results suggest that once water adsorbs on a metal surface, subsequent adsorption does not have a strong preference for the exposed metal surface and may equally condense on the water film.

